Supporting Information

Halogen Photoelimination from Monomeric Ni(III) Complexes Enabled by the Secondary Coordination Sphere

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A.1. Structural Data for $NiCl_2$(dppb) (9c)

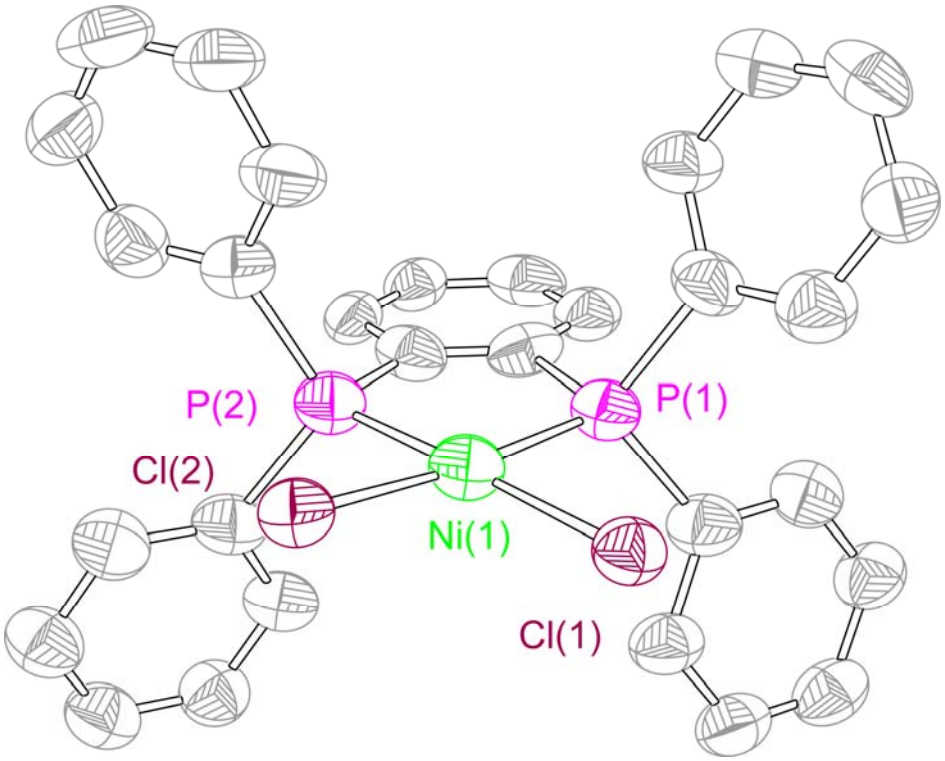

Figure S1. Thermal ellipsoid plot of $NiCl_2$(dppb) (**9c**) drawn at the 50% probability level. H-atoms and solvents are omitted for clarity.

Table S1. X-ray experimental details for $NiCl_2$(dppb) (**9c**) (CCDC 1401868)

Crystal Data	
Chemical formula	$C_{30}H_{24}Cl_2NiP_2$
Fw, g/mol	576.04
Crystal system, space group	Monoclinic, *Cc*
Temperature (K)	100(2)
a, *b*, *c* (Å)	15.0451(8), 9.6692(6), 18.4342(11)
α, β, γ (°)	90, 104.426(3), 90
V (Å^3)	2597.1(3)
Z	4
Radiation type	Cu *Kα*
μ (mm^{-1})	4.268
Crystal size (mm)	0.16 × 0.11 × 0.09
Data collection	
Diffractometer	Bruker APEX-II CCD
Absorption correction	Multi-scan, *SADABS*
T_{min}, T_{max}	0.5412, 0.6974
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17647, 3946, 3493
R_{int}	0.0825
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.610
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0861, 0.2240, 1.058
No. of reflections	3946
No. of parameters	317
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Dr_{max}, Dr_{min} (e Å^{-3})	1.258, –0.411

A.2. Structural Data for $NiBr_2$(dppe) (9e)

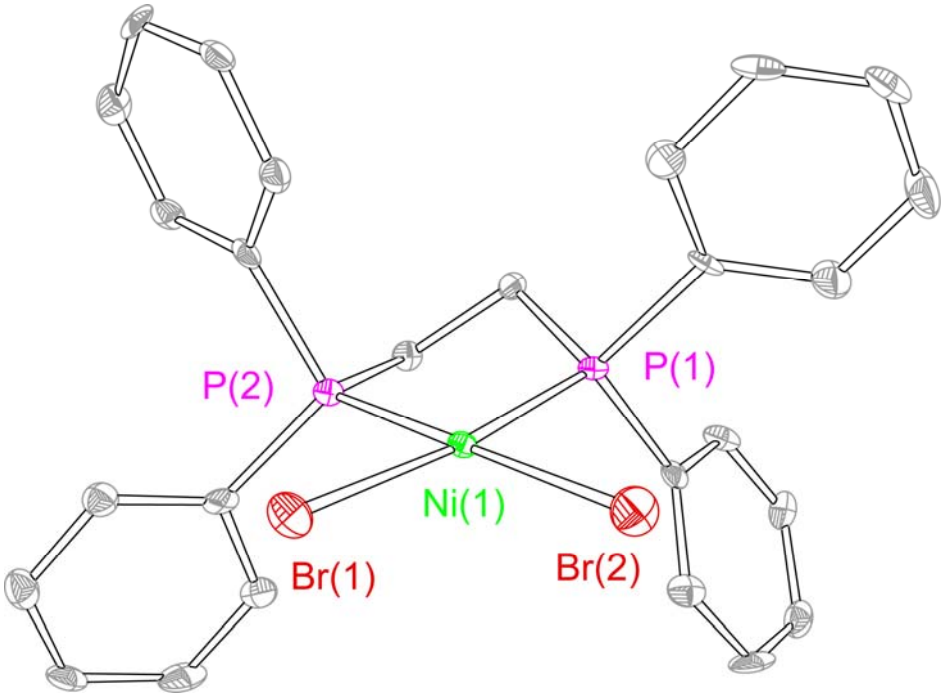

Figure S2. Thermal ellipsoid plot of $NiBr_2$(dppe) (**9e**) drawn at the 50% probability level. H-atoms and solvents are omitted for clarity.

Table S2. X-ray experimental details for complex $NiBr_2$(dppe) (**9e**) (CCDC 1401864)

Crystal Data	
Chemical formula	$C_{14}H_{14}BrCl_2\ Ni_{0.50}P$
Fw, g/mol	393.39
Crystal system, space group	Monoclinic, *P2(1)*
Temperature (K)	100(2)
a, *b*, *c* (Å)	13.0802(11), 8.5935(7), 13.7616(12)
α, β, γ (°)	90, 97.5170(14), 90
V (Å^3)	1533.6(2)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	3.709
Crystal size (mm)	0.46 × 0.02 × 0.02
Data collection	
Diffractometer	Bruker APEX-II CCD
Absorption correction	Multi-scan, *SADABS*
T_{min}, T_{max}	0.2802, 0.9295
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17572, 5280, 4788
R_{int}	0.0552
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.610
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0397, 0.0960, 1.051
No. of reflections	5280
No. of parameters	334
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Dr_{max}, Dr_{min} (e Å^{-3})	1.416, –0.790

B. Electrochemical Data

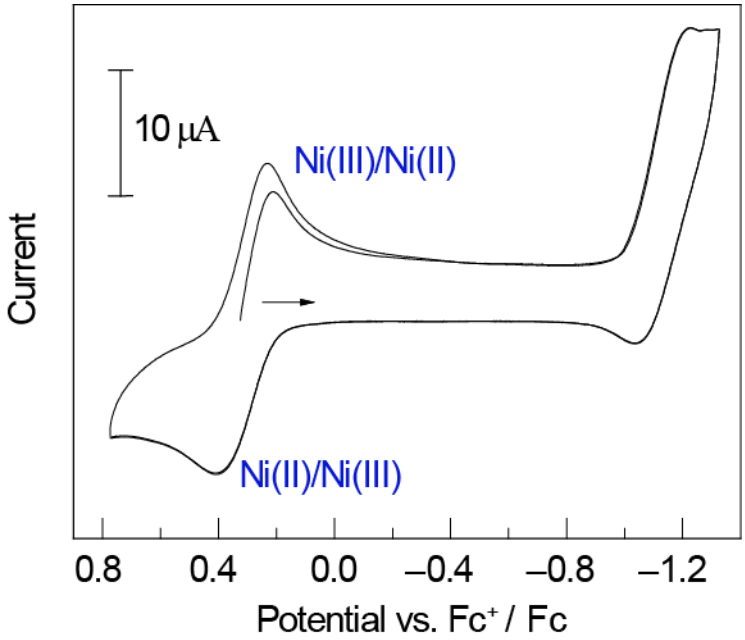

Figure S3. Cyclic voltammogram of 1 mM CH_3CN solution of $NiCl_3$(dppe) (**7a**), with 0.1 M $^nBu_4PF_6$ as the supporting electrolyte. Data was recorded at a scan rate of 100 mV/s with a glassy carbon working electrode, $Ag/AgNO_3$ reference, and Pt wire counter electrode.

C. EPR Spectroscopy

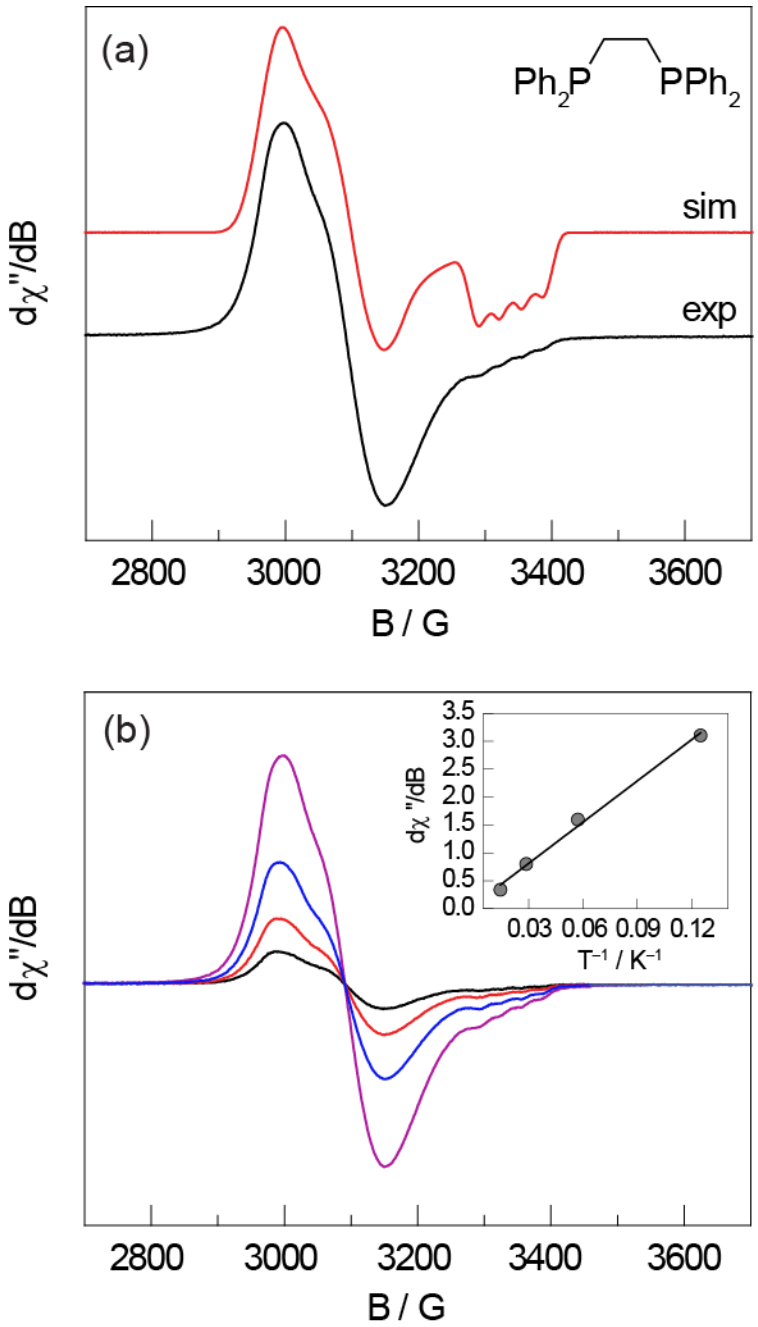

Figure S4. (a) EPR spectrum of $NiCl_3$(dppe) (**7a**) recorded at 8.0 K in 1:1 CH_3CN/toluene glass (—, black) and simulated (—, red). (b) EPR spectra of a frozen solution of $NiCl_3$(dppe) (**7a**) in 1:1 CH_3CN/toluene obtained at 70.0 K (—, black) 35.0 K (—, red), 17.5 K (—, blue), and 8.0 K (—, purple). Inset: plot of intensity at 2997 G versus inverse temperature.

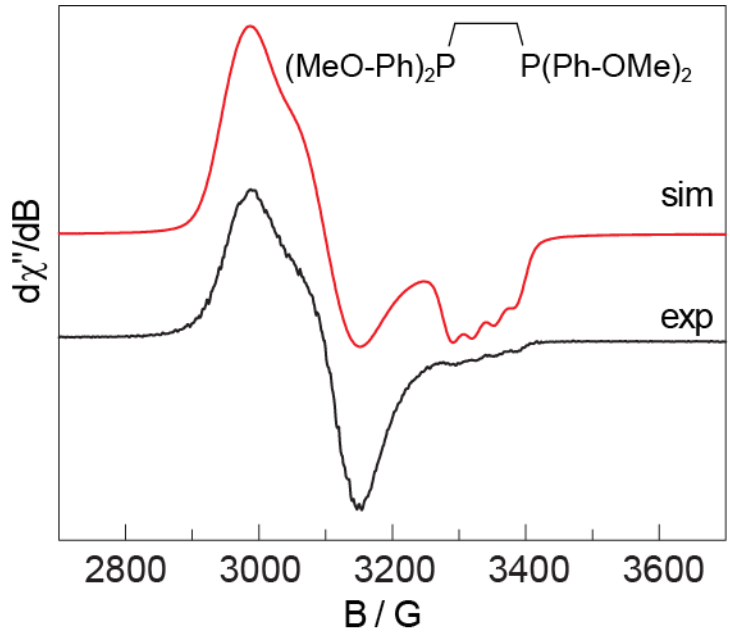

Figure S5. EPR spectrum of $NiCl_3$(dppe-OMe) (**7a-OMe**) recorded at 77 K in 1:1 DCM/toluene glass (—, black) and simulated (—, red).

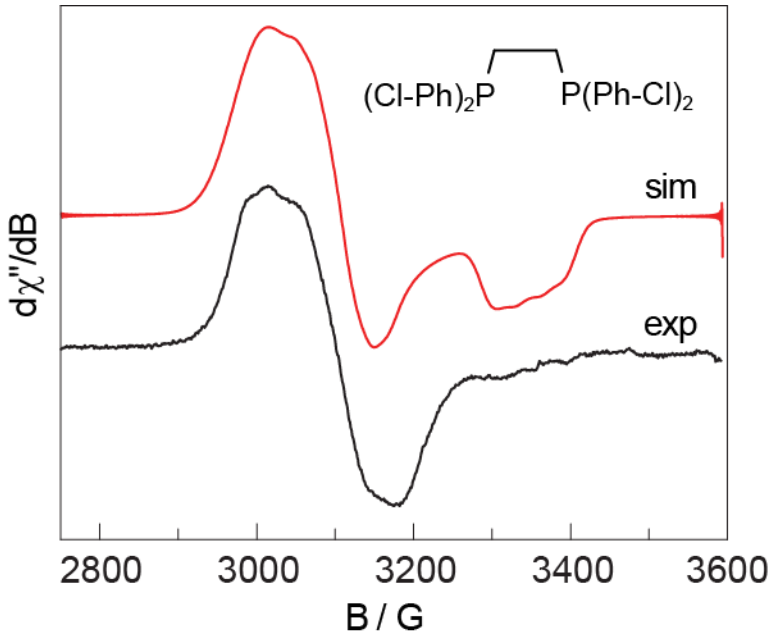

Figure S6. EPR spectrum of $NiCl_3$(dppe-Cl) (**7a-Cl**) recorded at 77 K in 1:1 DCM/toluene glass (—, black) and simulated (—, red). For the simulation, the axial hyperfine, $|A_z|$, was fixed to 90 MHz and not optimized.

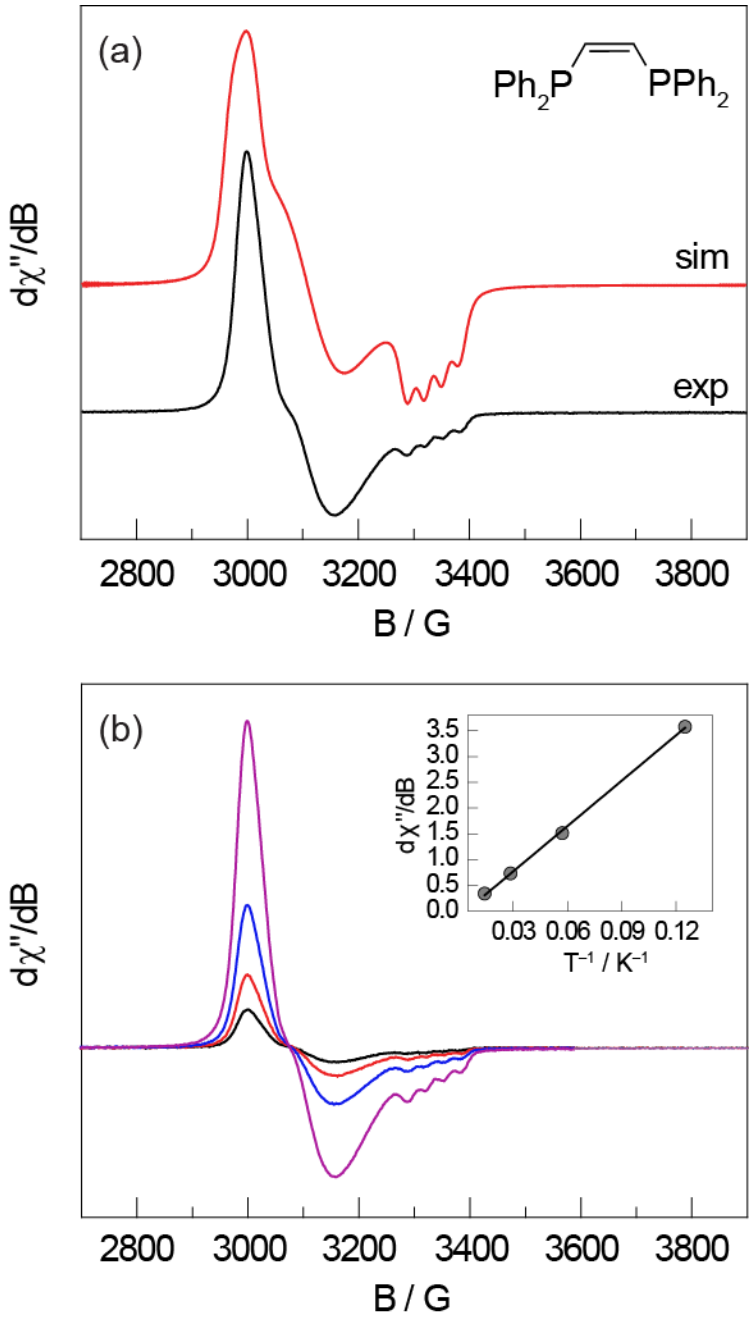

Figure S7. (a) EPR spectrum of $NiCl_3$(dppey) (**7b**) recorded at 8.0 K in 1:1 CH_3CN/toluene glass (—, black) and simulated (—, red). (b) EPR spectra of a frozen solution of $NiCl_3$(dppey) (**7b**) in 1:1 CH_3CN/toluene obtained at 70.0 K (—, black) 35.0 K (—, red), 17.5 K (—, blue), and 8.0 K (—, purple). Inset: plot of intensity at 2999 G versus inverse temperature.

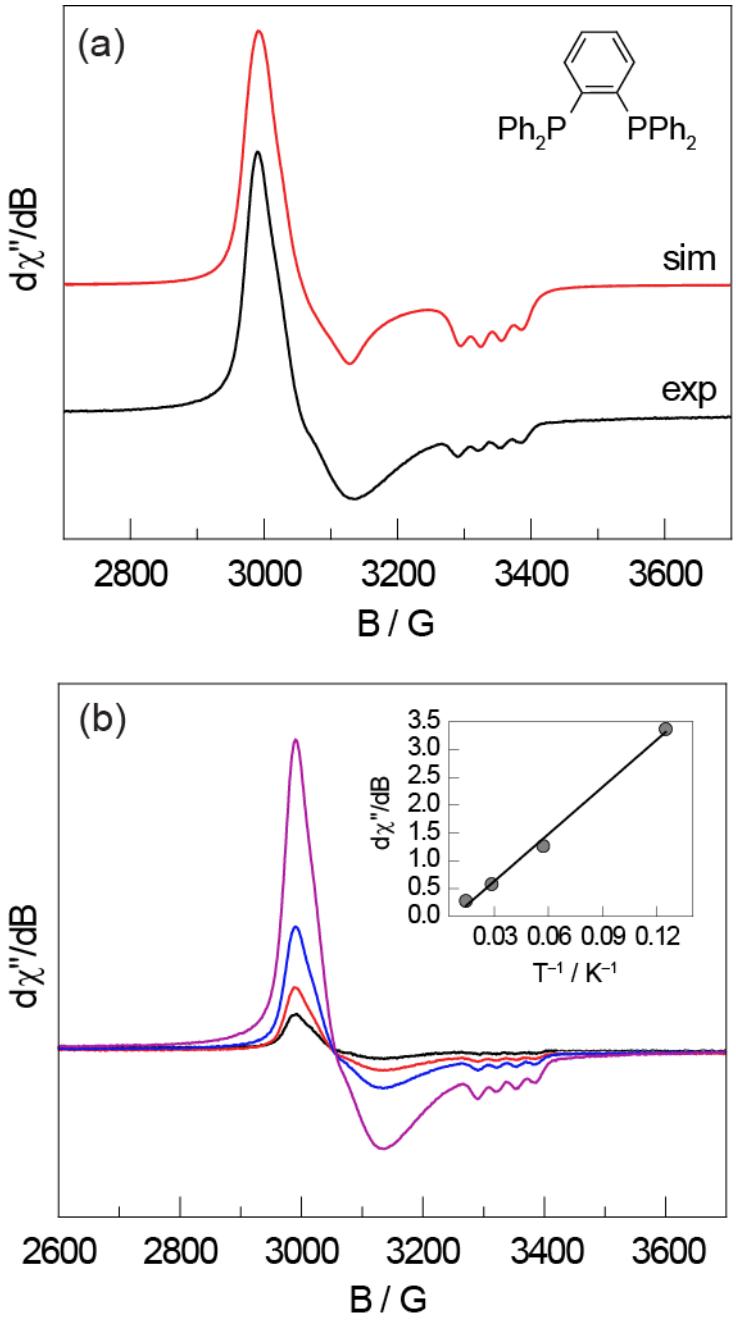

Figure S8. (a) EPR spectrum of $NiCl_3$(dppb) (**7c**) recorded at 8.0 K in 1:1 CH_3CN/toluene glass (—, black) and simulated (—, red). (b) EPR spectra of a frozen solution of $NiCl_3$(dppb) (**7c**) in 1:1 CH_3CN/toluene obtained at 70.0 K (—, black) 35.0 K (—, red), 17.5 K (—, blue), and 8.0 K (—, purple). Inset: plot of intensity at 2990 G versus inverse temperature.

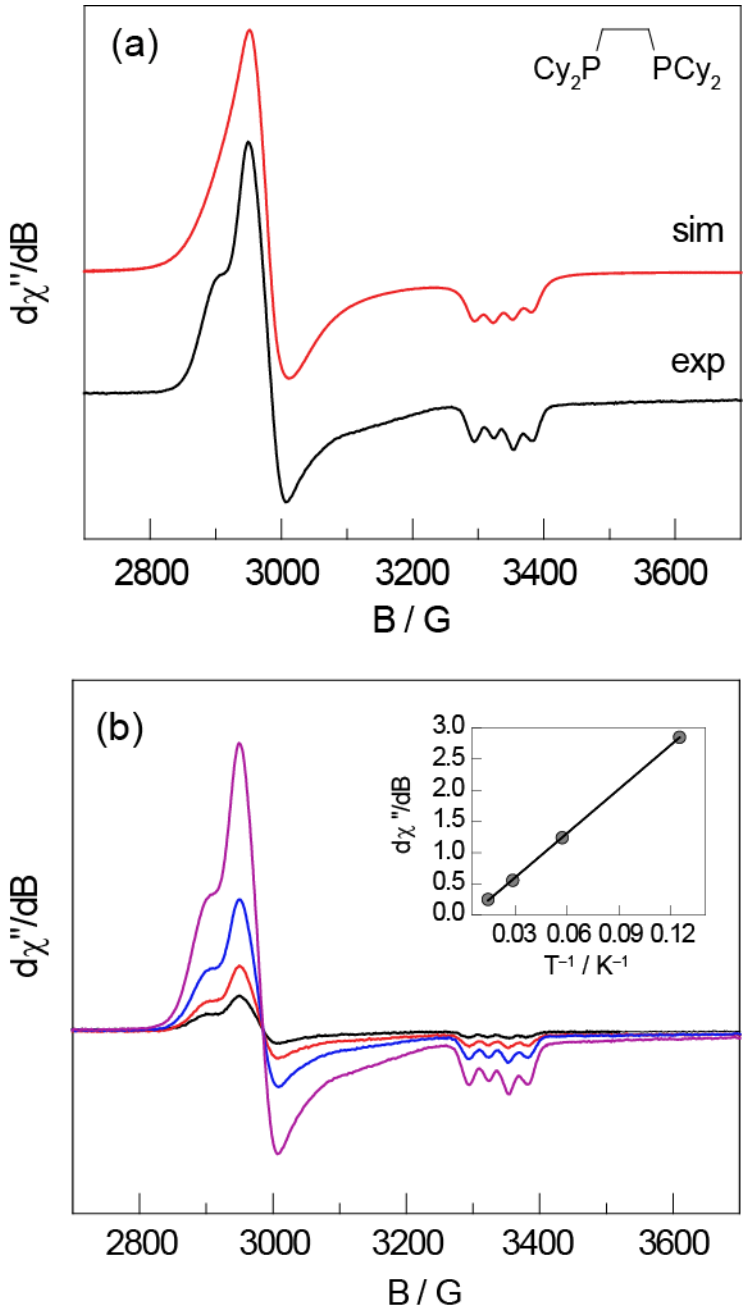

Figure S9. (a) EPR spectrum of $NiCl_3$(dcpe) (**7d**) recorded at 8.0 K in 1:1 CH_3CN/toluene glass (—, black) and simulated (—, red). (b) EPR spectra of a frozen solution of $NiCl_3$(dcpe) (**7d**) in 1:1 CH_3CN/toluene obtained at 70.0 K (—, black) 35.0 K (—, red), 17.5 K (—, blue), and 8.0 K (—, purple). Inset: plot of intensity at 2950 G versus inverse temperature.

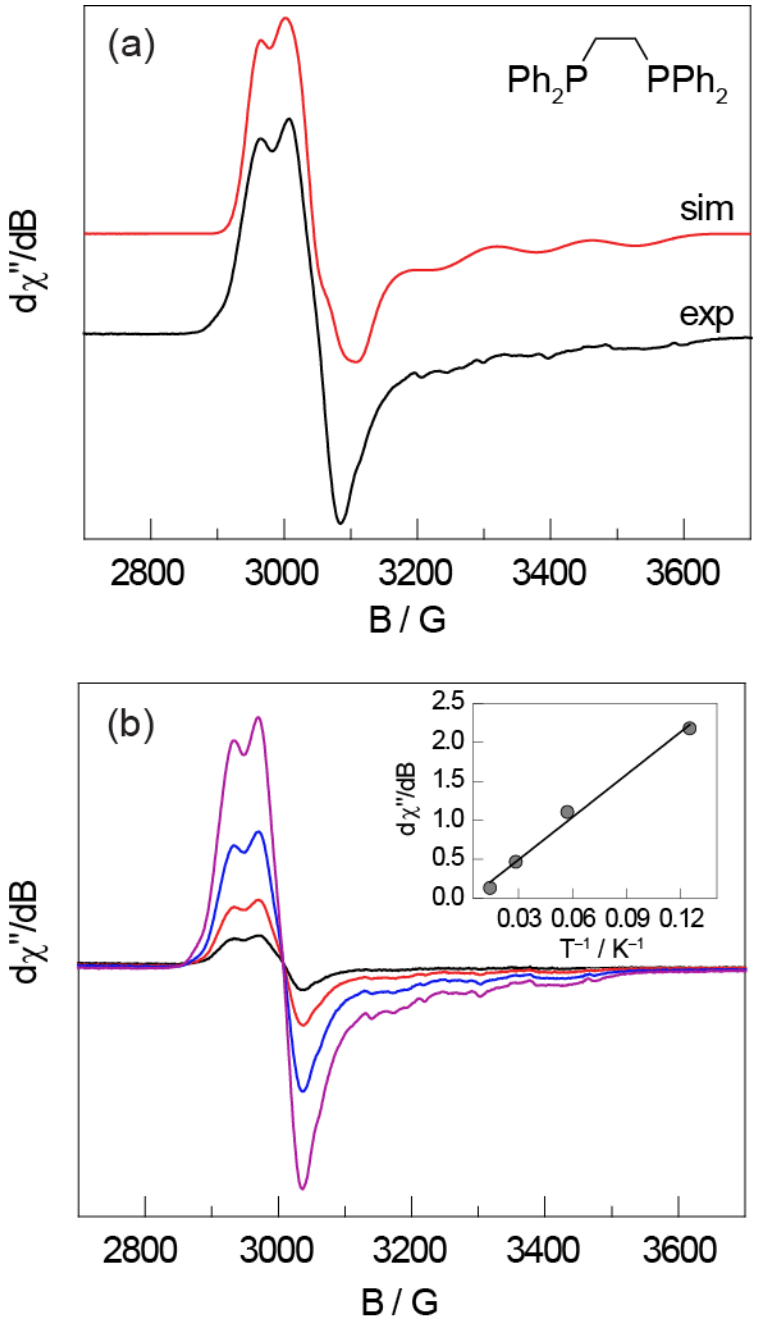

Figure S10. (a) EPR spectrum of $NiBr_3$(dppe) (**7e**) recorded at 8.0 K in 1:1 DCM/toluene glass (—, black) and simulated (—, red). (b) EPR spectra of a frozen solution of $NiBr_3$(dppe) (**7e**) in 1:1 DCM/toluene obtained at 70.0 K (—, black) 35.0 K (—, red), 17.5 K (—, blue), and 8.0 K (—, purple). Inset: plot of intensity at 2970 G versus inverse temperature.

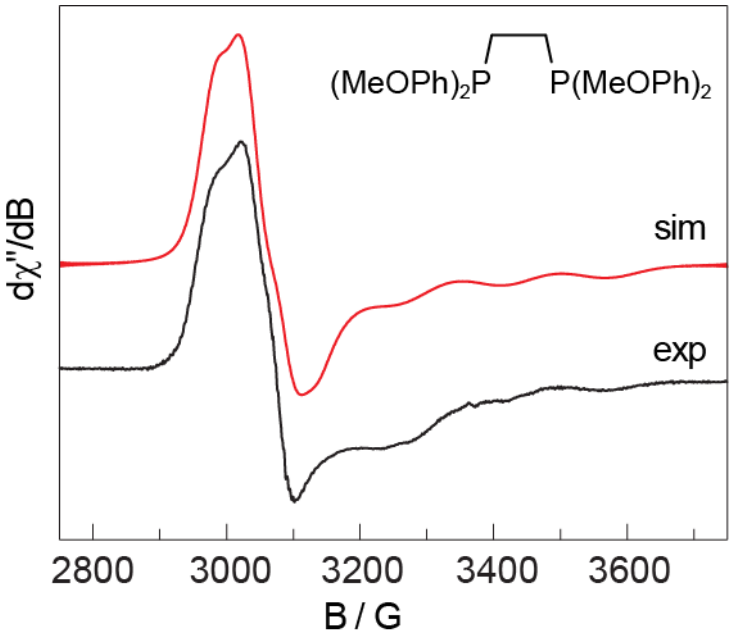

Figure S11. EPR spectrum of $NiBr_3$(dppe) (**7e-OMe**) recorded at 77.0 K in 1:1 DCM/toluene glass (—, black) and simulated (—, red).

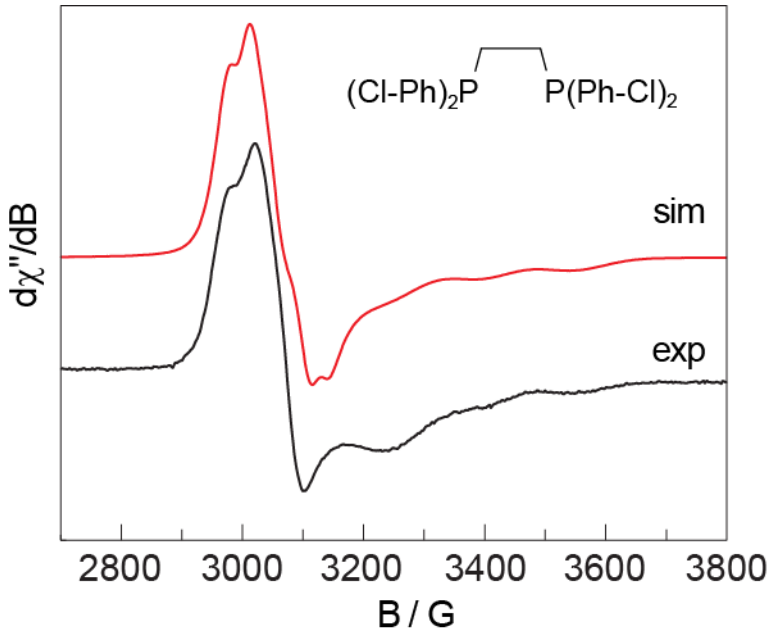

Figure S12. EPR spectrum of $NiBr_3$(dppe-Cl) (**7e-Cl**) recorded at 77.0 K in 1:1 DCM/toluene glass (—, black) and simulated (—, red).

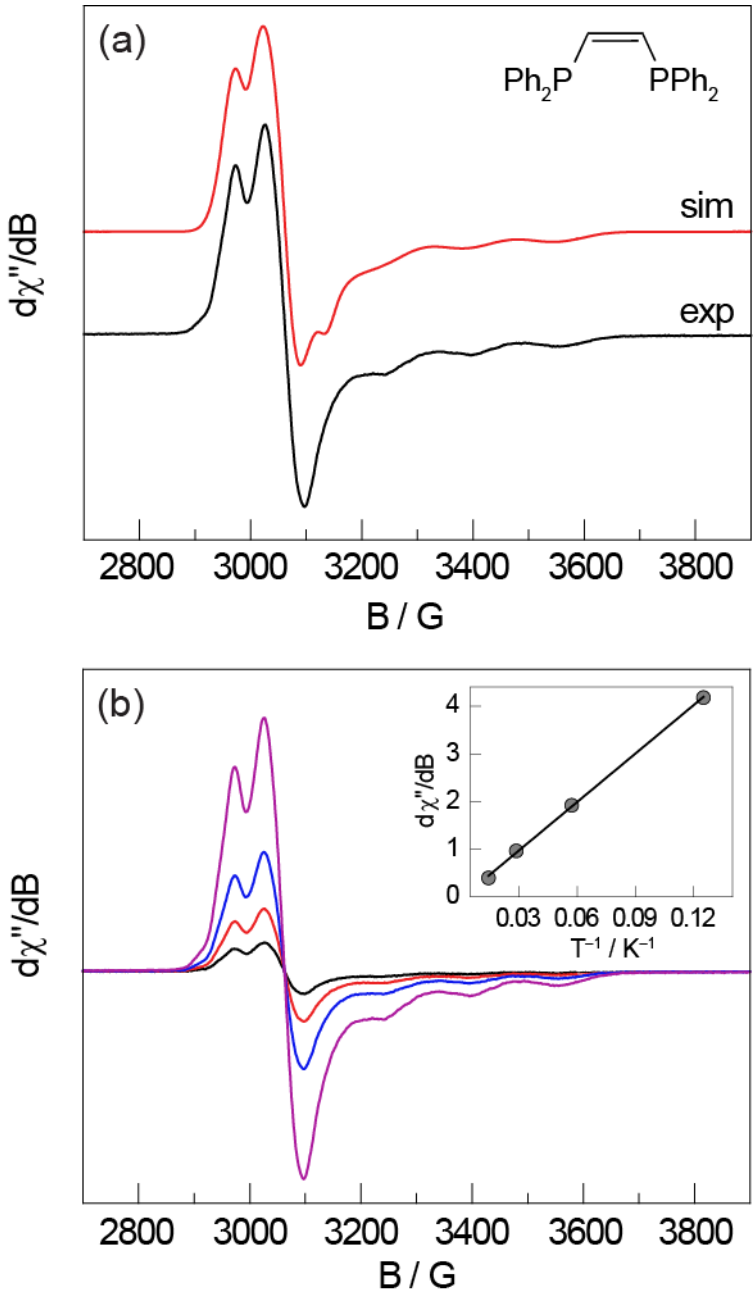

Figure S13. (a) EPR spectrum of $NiBr_3$(dppey) (**7f**) recorded at 8.0 K in 1:1 DCM/toluene glass (—, black) and simulated (—, red). (b) EPR spectra of a frozen solution of $NiBr_3$(dppey) (**7f**) in 1:1 DCM/toluene obtained at 70.0 K (—, black) 35.0 K (—, red), 17.5 K (—, blue), and 8.0 K (—, purple). Inset: plot of intensity at 3025 G versus inverse temperature.

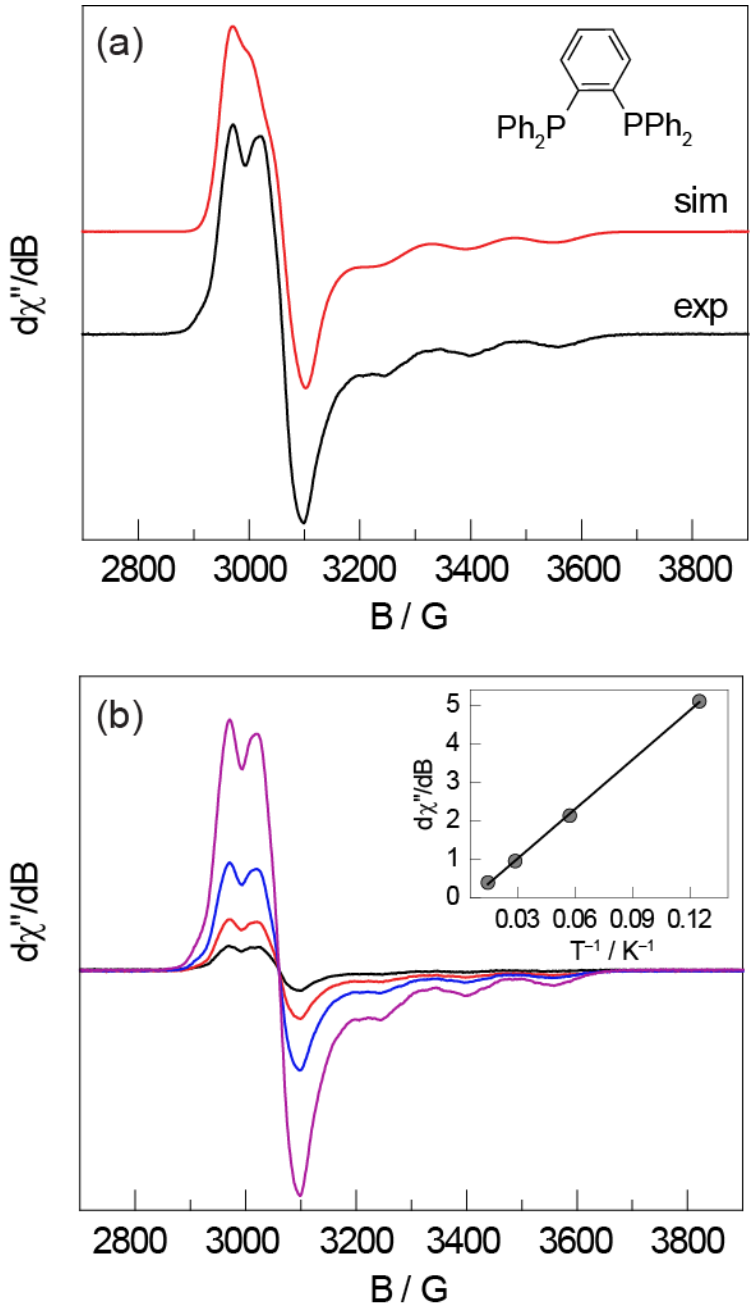

Figure S14. (a) EPR spectrum of $NiBr_3$(dppb) (**7g**) recorded at 8.0 K in 1:1 DCM/toluene glass (—, black) and simulated (—, red). (b) EPR spectra of a frozen solution of $NiBr_3$(dppb) (**7g**) in 1:1 DCM/toluene obtained at 70.0 K (—, black) 35.0 K (—, red), 17.5 K (—, blue), and 8.0 K (—, purple). Inset: plot of intensity at 2971 G versus inverse temperature.

Table S3. EPR parameters derived from fitting of $NiX_3(LL)$ (**7**) spectra.

Compound	g_x	g_y	g_z	$\|A_z\|$/MHz
7a: $NiCl_3$(dppe)	2.245	2.164	2.012	95
7a-OMe: $NiCl_3$(dppe-OMe)	2.258	2.169	2.017	95
7a-Cl: $NiCl_3$(dppe-Cl)	2.241	2.165	2.01	–
7b: $NiCl_3$(dppey)	2.241	2.155	2.013	92
7c: $NiCl_3$(dppb)	2.232	2.196	2.010	92
7d: $NiCl_3$(dcpe)	2.280	2.260	2.010	81
7e: $NiBr_3$(dppe)	2.203	2.203	2.025	400
7e-OMe: $NiBr_3$(dppe-OMe)	2.208	2.208	2.025	420
7e-Cl: $NiBr_3$(dppe-Cl)	2.201	2.191	2.025	410
7f: $NiBr_3$(dppey)	2.192	2.187	2.024	430
7g: $NiBr_3$(dppb)	2.226	2.176	2.020	420

Table S4. Selected metrical parameters of $NiBr_3(LL)$ complexes **7e-7g** derived from X-ray diffraction data.

LL	Ni–Br_{ap} (Å)	Ni–Br_{basal} (Å)	P1–Ni–P2 (°)	Planarity (°)[a]
dppe	2.4004(10)	2.3625	83.63(6)	34.91
dppey	2.4428(10)	2.3613	87.52(5)	28.87
dppb	2.4410(9)	2.3672	83.64(3)	33.74

[a] 360-(two Br_{ap}–Ni–Br_{basal} + two Br_{ap}–Ni–P_{basal}) (°).

D. Steady-State Photolysis Experiments

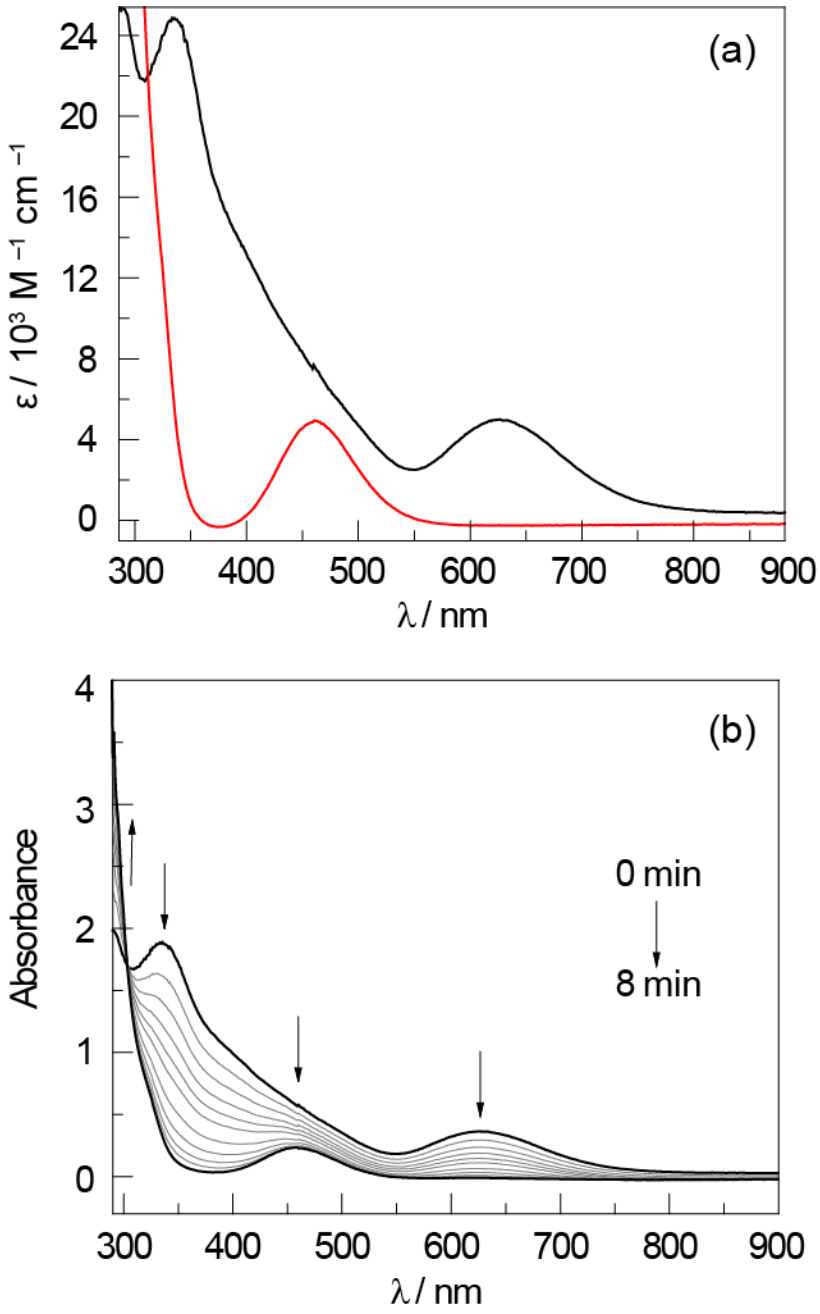

Figure S15. (a) Extinction spectra of $NiCl_3$(dppe-Cl) (**7a-Cl**) (—, black) and $NiCl_2$(dppe-Cl) (**9a-Cl**) (—, red). (b) Spectral evolution for the photolysis of $NiCl_3$dppe-Cl (**7a-Cl**) in MeCN (λ_{exc} > 400 nm).

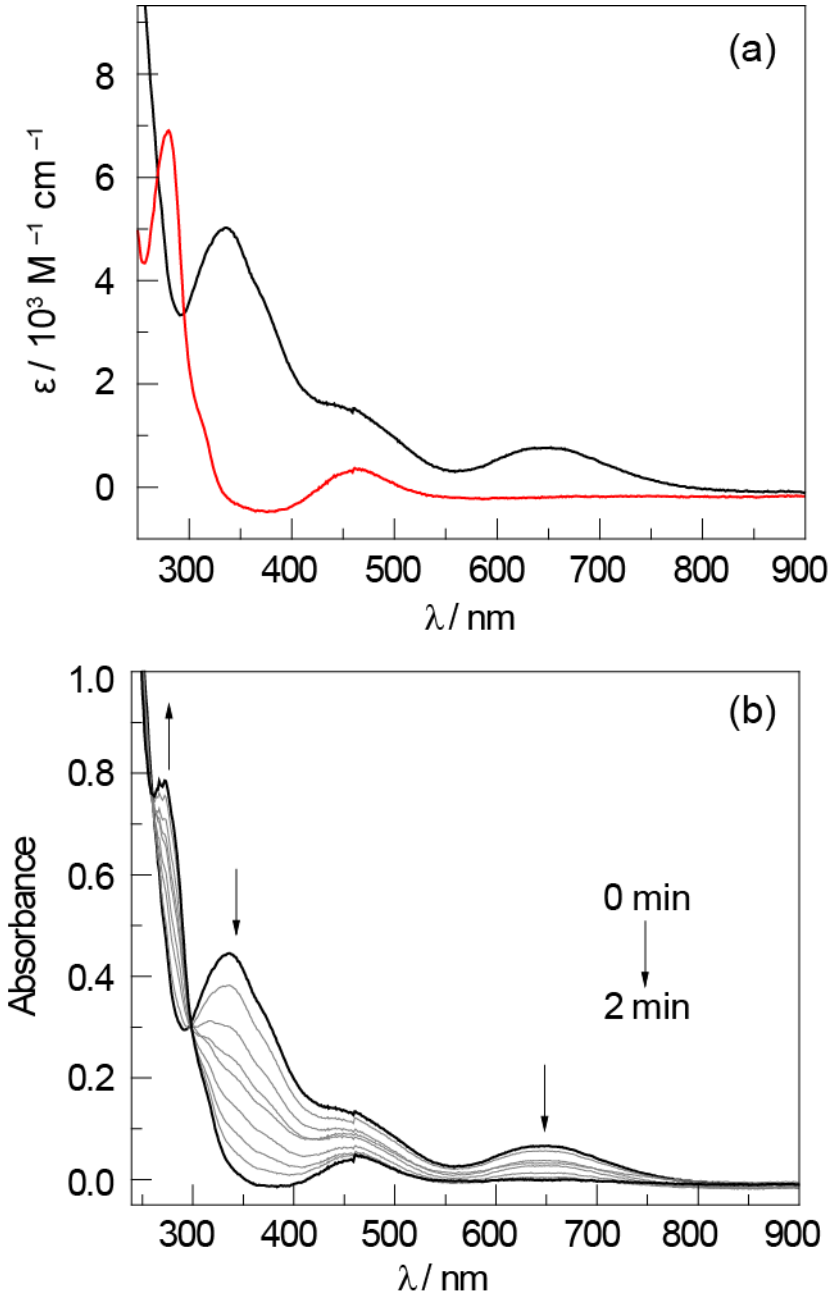

Figure S16. (a) Extinction spectra of $NiCl_3$(dppey) (**7b**) (—, black) and $NiCl_2$(dppey) (**9b**) (—, red). (b) Spectral evolution for the photolysis of complex $NiCl_3$(dppey) (**7b**) in MeCN (λ_{exc} > 400 nm).

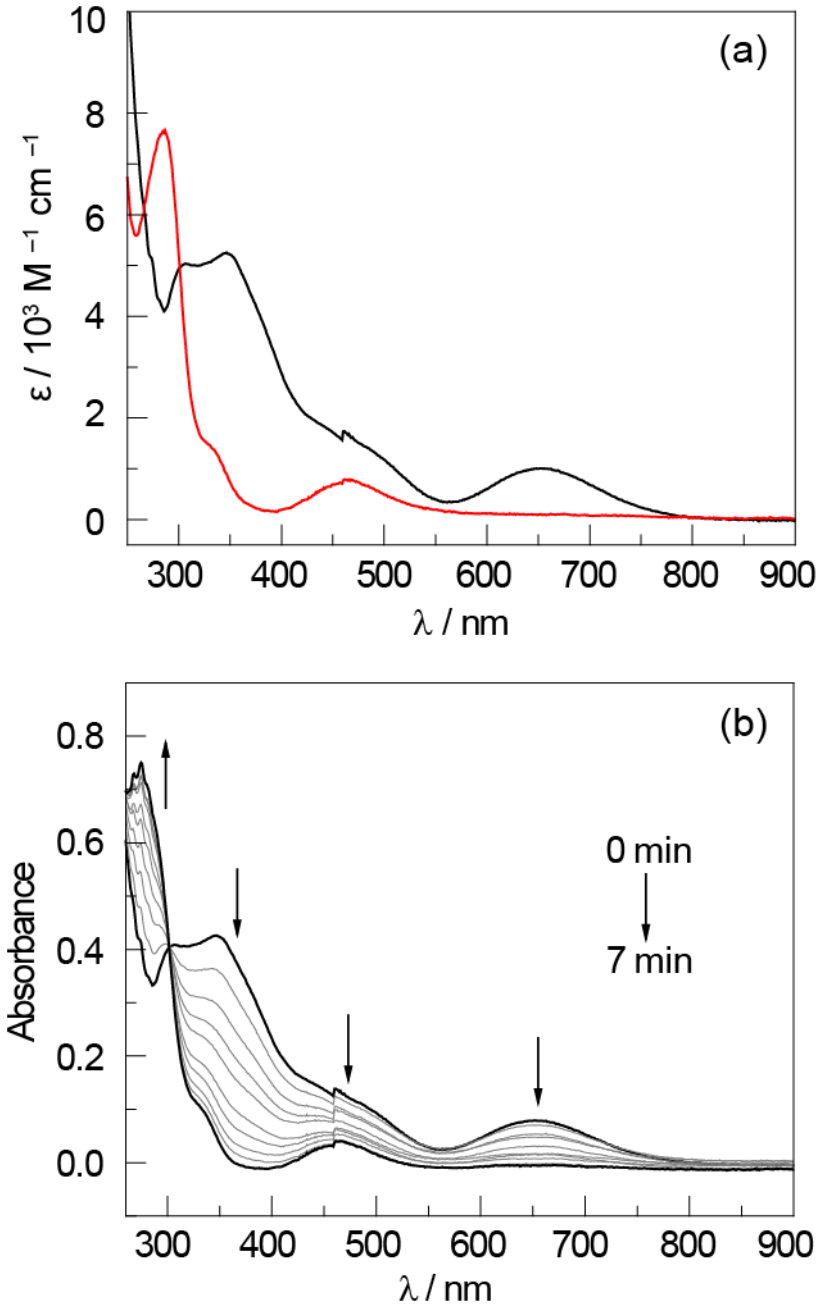

Figure S17. (a) Extinction spectra of $NiCl_3$(dppb) (**7c**) (—, black) and $NiCl_2$(dppb) (**9c**) (—, red). (b) Spectral evolution for the photolysis of $NiCl_3$(dppb) (**7c**) in MeCN (λ_{exc} > 400 nm).

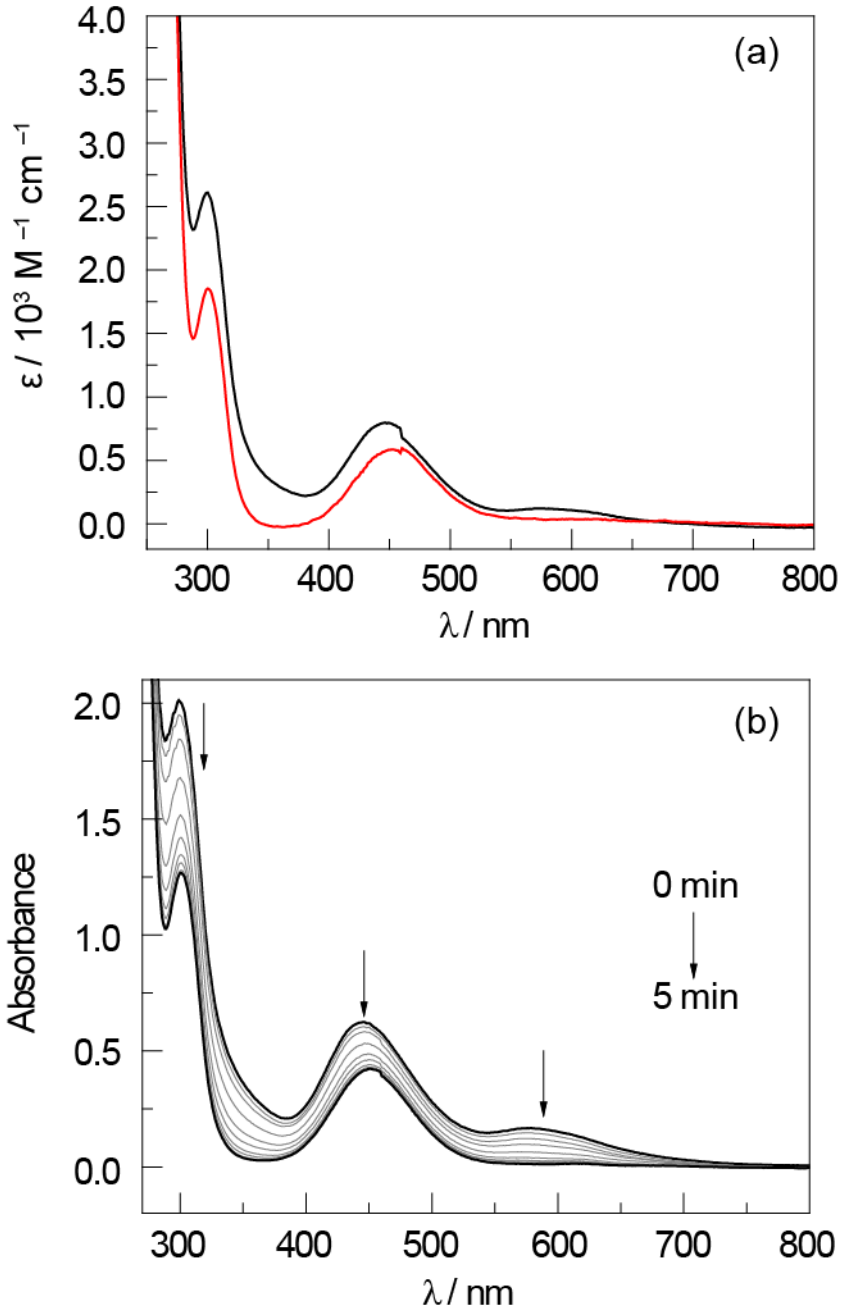

Figure S18. (a) Extinction spectra of $NiCl_3$(dcpe) (**7d**) (—, black) and $NiCl_2$(dcpe) (**9d**) (—, red). (b) Spectral evolution for the photolysis of $NiCl_3$(dcpe) (**7d**) in MeCN (λ_{exc} > 400 nm).

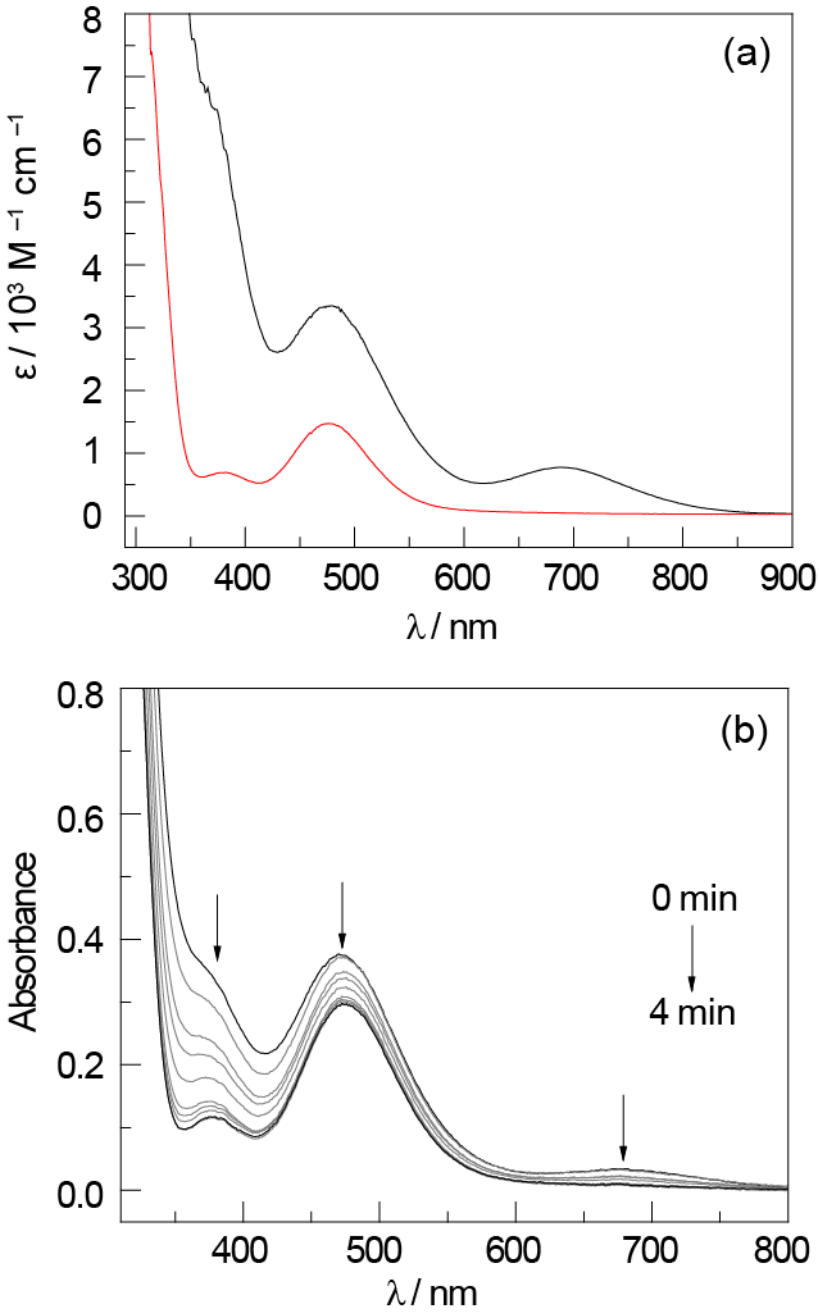

Figure S19. (a) Extinction spectra of $NiBr_3(dppe)$ (**7e**) (—, black) and $NiBr_2(dppe)$ (**9e**) (—, red). (b) Spectral evolution for the photolysis of $NiBr_3(dppe)$ (**7e**) in CH_2Cl_2 (λ_{exc} > 400 nm).

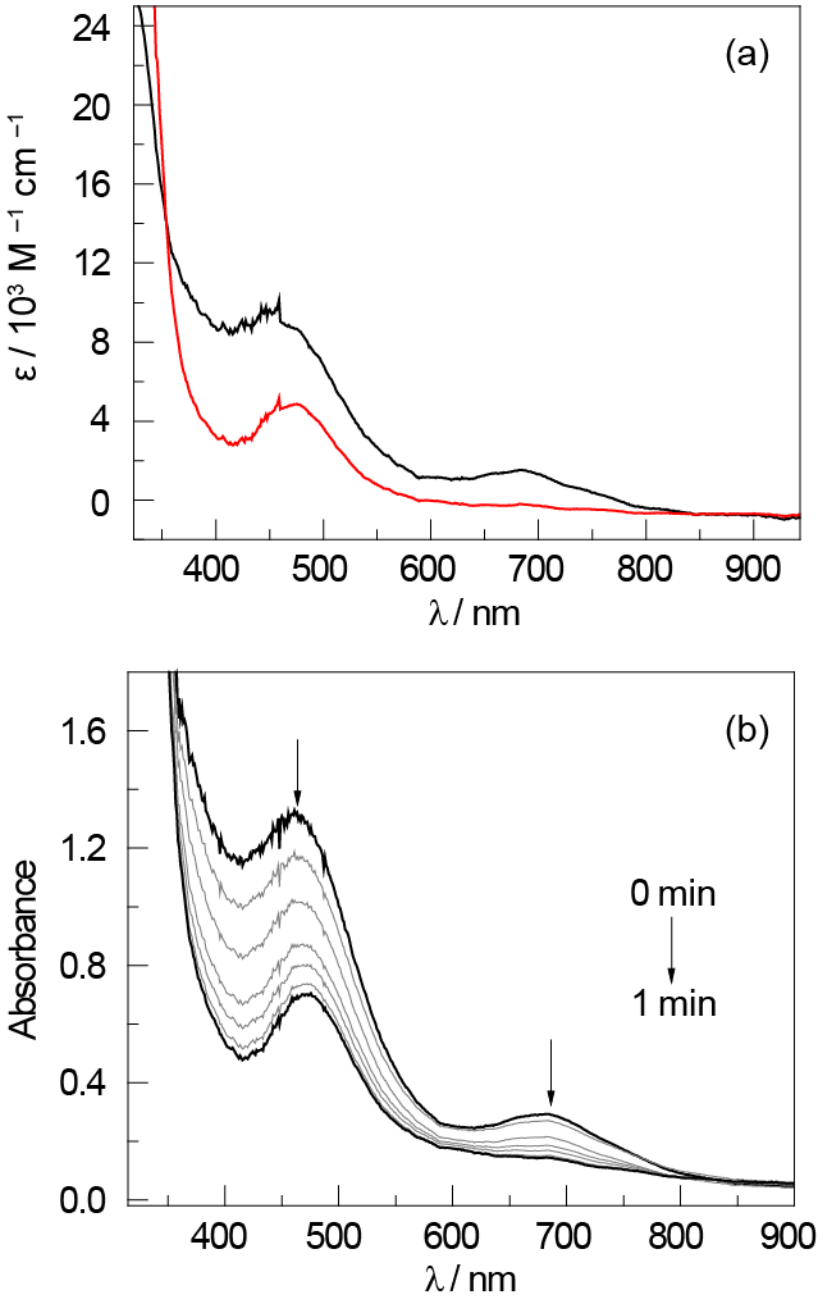

Figure S20. (a) Extinction spectra of $NiBr_3$(dppe-OMe) (**7e-OMe**) (—, black) and $NiBr_2$(dppe-OMe) (**9e-OMe**) (—, red). (b) Spectral evolution for the photolysis of $NiBr_3$(dppe-OMe) (**7e-OMe**) in CH_2Cl_2 (λ_{exc} > 400 nm).

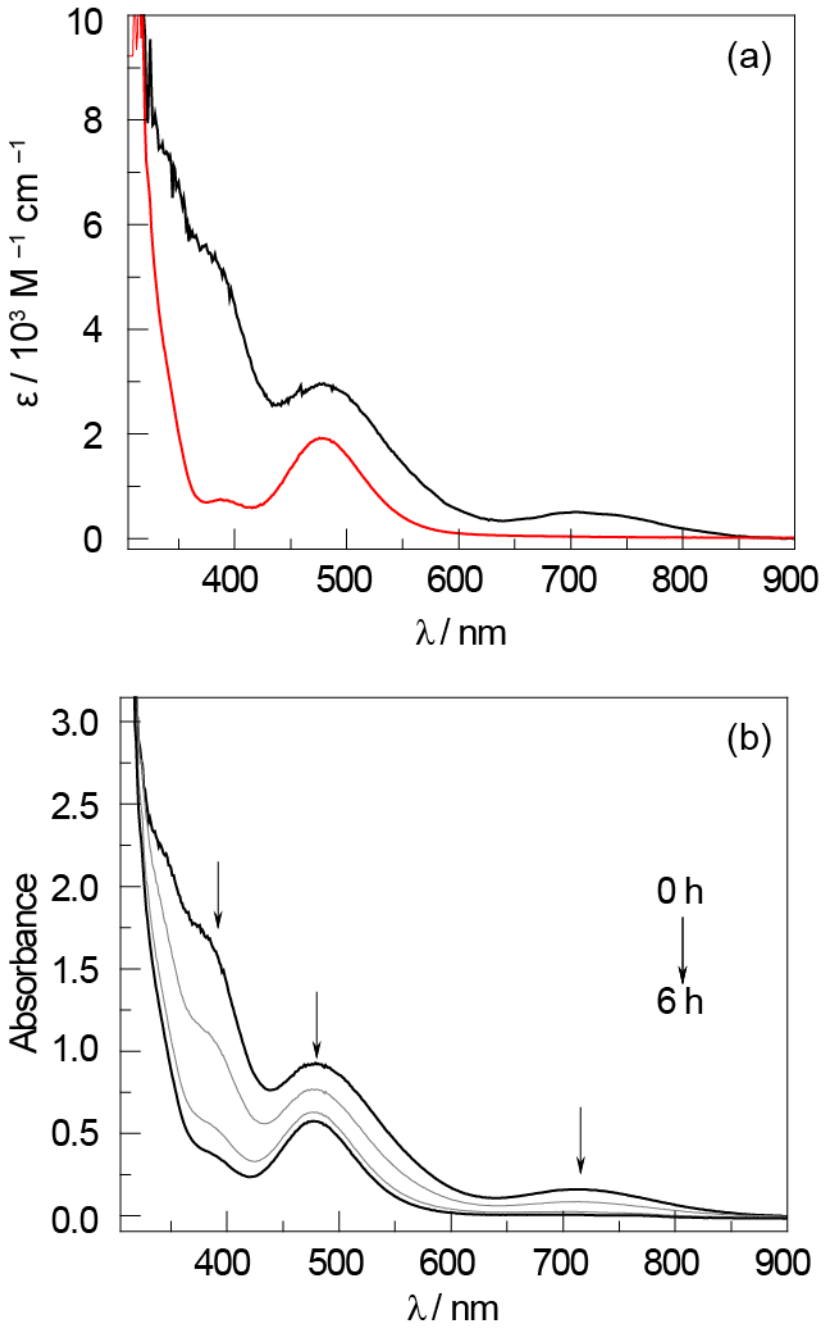

Figure S21. (a) Extinction spectra of $NiBr_3$(dppb) (**7g**) (—, black) and $NiBr_2$(dppb) (**9g**) (—, red). (b) Spectral evolution for the photolysis $NiBr_3$(dppb) (**7g**) in CH_2Cl_2 (λ_{exc} > 400 nm).

Table S5. UV-vis spectral absorption maxima of LMCT transitions

LL	$NiCl_3$(LL)	λ_{max} LMCT / nm		$NiBr_3$(LL)	λ_{max} LMCT / nm
dppe	**7a**	452, 622		**7e**	472, 682
dppe-OMe	**7a-OMe**	430, 618		**7e-OMe**	462, 680
dppe-Cl	**7a-Cl**	336, 627		**7e-Cl**	478, 691
dppey	**7b**	441, 649		**7f**	476, 699
dppb	**7c**	453, 652		**7g**	479, 715
dcpe	**7d**	446, 586			

E. NMR Data

Complexes **9b**[1] and **9f**[2] have been previously reported, but only $^{31}P\{^{1}H\}$ NMR data has been reported. Complexes **9c**[3] has been reported in the literature but neither ^{1}H or $^{31}P\{^{1}H\}$ NMR data have been reported.

$NiCl_2$(dppe-Cl) (**9a-Cl**): ^{1}H NMR (600 MHz, CD_2Cl_2) δ (ppm): 7.89 (m, 8H), 7.54 (d, $^{3}J_{HH}$ = 7.8 Hz, 8H), 2.15 (d, J_{HP} = 17.4 Hz, 4H); $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2) δ (ppm): 56.7 (s).

$NiCl_2$(dppey) (**9b**): ^{1}H NMR (600 MHz, CD_2Cl_2) δ (ppm): 7.89 (m, 7H), 7.61 (m, 2H), 7.52 (m, 7H), 6.68 (m, 2H); $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2) δ (ppm): 64.7 (s).

$NiCl_2$(dppb) (**9c**): ^{1}H NMR (600 MHz, CD_2Cl_2) δ (ppm): 7.85 (m, 6H), 7.58 (m, 4H), 7.47 (m, 8H), 7.29 (m, 3H), 6.96 (m, 3H); $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2) δ (ppm): 57.3 (s).

$NiBr_2$(dppe-Cl) (**9e-Cl**): ^{1}H NMR (600 MHz, CD_2Cl_2) δ (ppm): 7.88 (m, 8H), 7.55(d, $^{3}J_{HH}$ = 8.4 Hz, 8H), 2.12 (d, J_{HP} = 17.4 Hz, 4H); $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2) δ (ppm): 65.2 (s).

$NiBr_2$(dppey) (**9f**): ^{1}H NMR (600 MHz, CD_2Cl_2) δ (ppm): 7.90 (m, 8H), 7.60 (m, 3H), 7.52 (m, 4H), 6.83 (m, 2H); $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2) δ (ppm): 73.6 (s).

$NiBr_2$(dppb) (**9g**): ^{1}H NMR (600 MHz, CD_2Cl_2) δ (ppm): 7.75 (m, 4H), 7.62 (m, 8H), 7.25 (m, 10H), 7.00 (m, 4H). $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2) δ (ppm): 65.2 (s).

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1 Bomfim, J. A. S.; de Souza, F. P.; Filgueiras, C. A. L.; de Sousa, A. G.; Gambardella, M. T. P. *Polyhedron*, **2003**, *22*, 1567.

2 Jarrett, P. S.; Sadler, P. J. *Inorg. Chem.* **1991**, *30*, 2098.

3 Smeets, B. J. J.; Meijer, R. H.; Meuldijk, J.; Vekemans, J. A. J. M.; Hulshof, L. A. *Org. Proc. Res. Dev*. **2003**, *7*, 10.

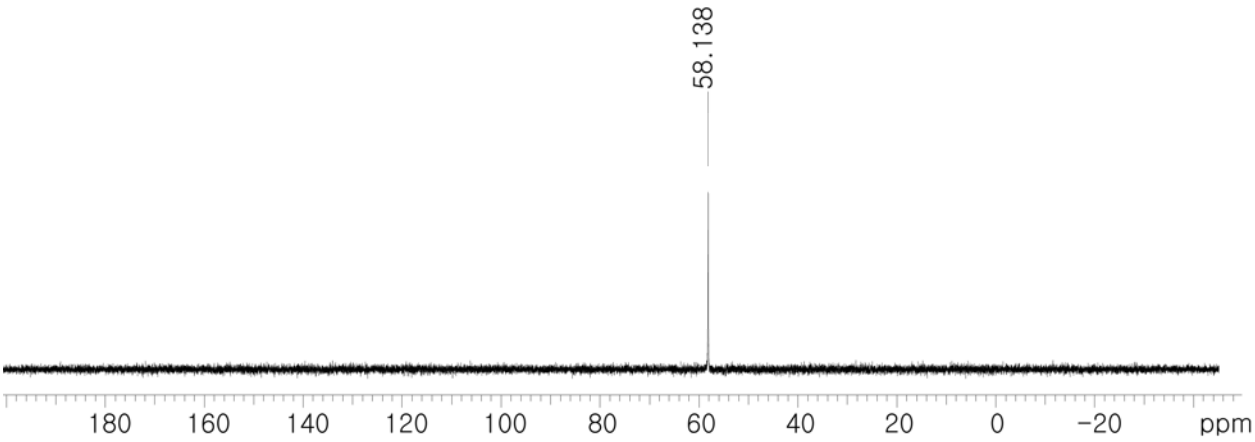

Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution obtained by photolysis of $NiCl_3$(dppe) (**7a**) with visible light (λ > 400 nm) recorded in CD_2Cl_2 at 23 °C.

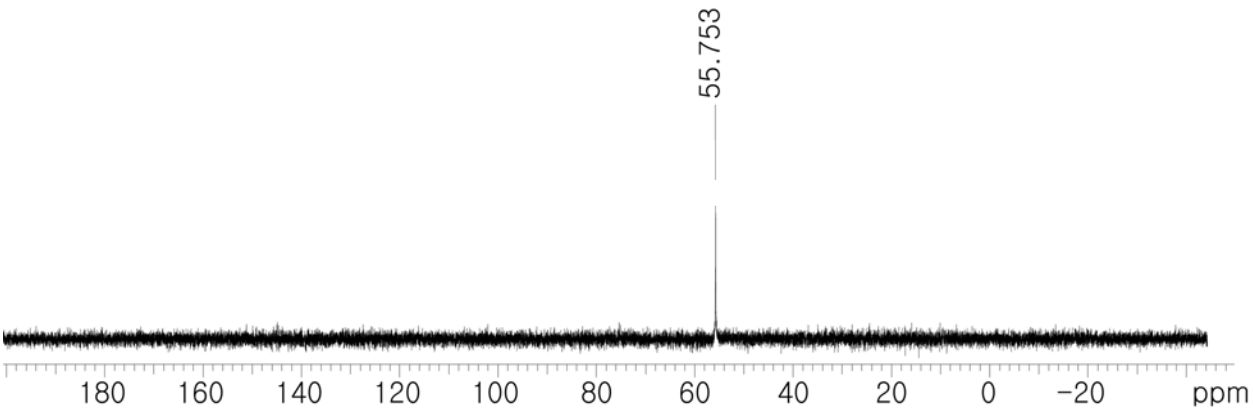

Figure S23. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution obtained by photolysis of $NiCl_3$(dppe-OMe) (**7a-OMe**) with visible light (λ > 400 nm) recorded in CD_2Cl_2 at 23 °C.

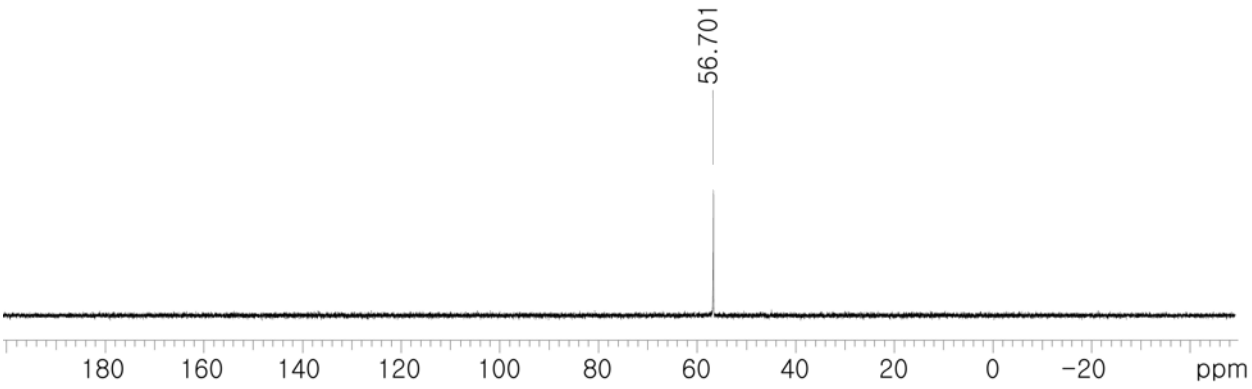

Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution obtained by photolysis of $NiCl_3$(dppe-Cl) (**7a-Cl**) with visible light (λ > 400 nm) recorded in CD_2Cl_2 at 23 °C.

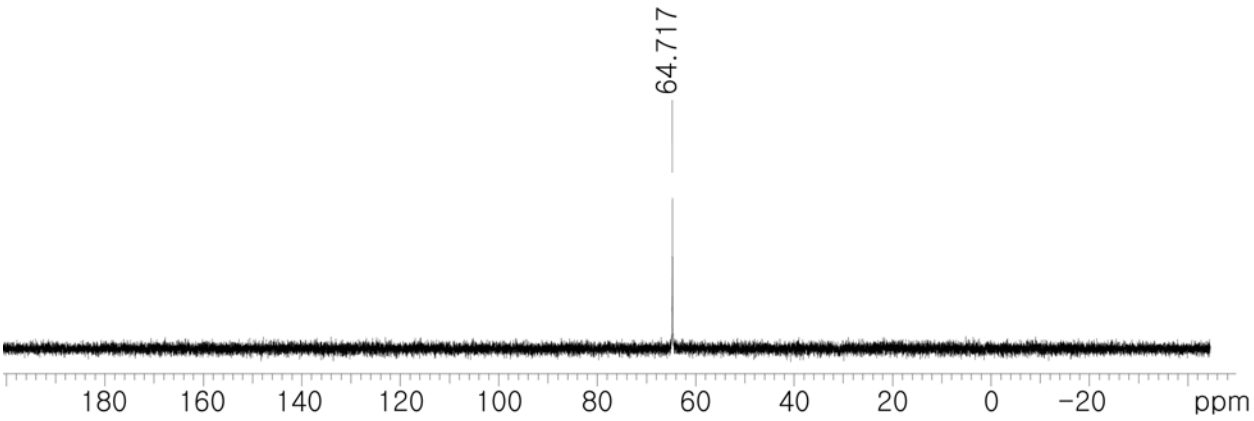

Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution obtained by photolysis of $NiCl_3$(dppey) (**7b**) with visible light (λ > 400 nm) recorded in CD_2Cl_2 at 23 °C.

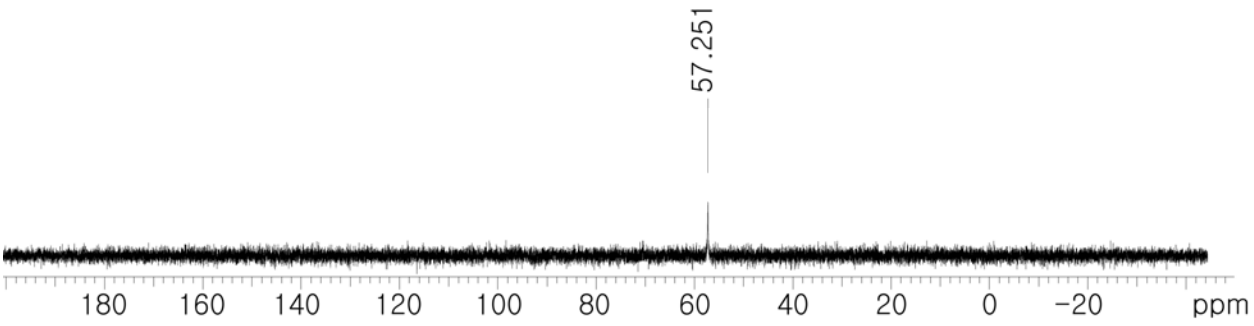

Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution obtained by photolysis of $NiCl_3$(dppb) (**7c**) with visible light (λ > 400 nm) recorded in CD_2Cl_2 at 23 °C.

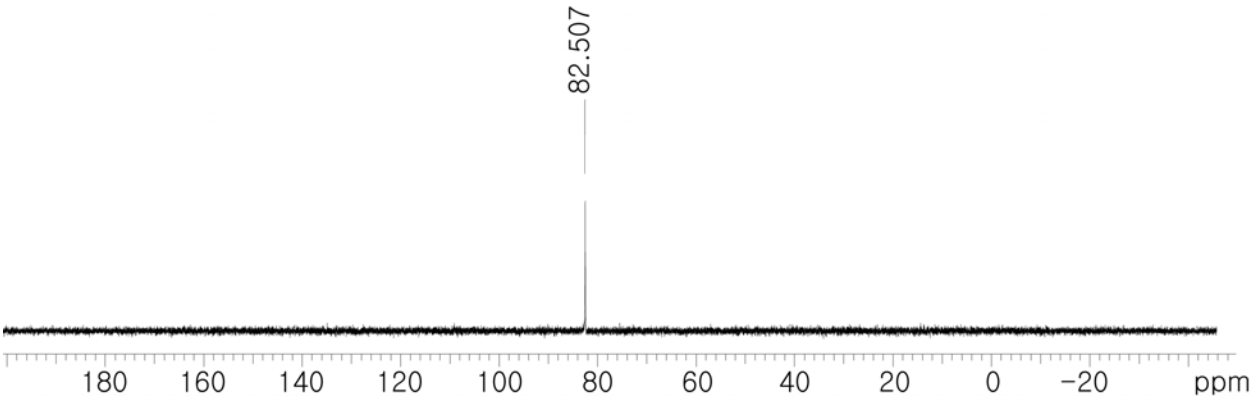

Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution obtained by photolysis of $NiCl_3$(dcpe) (**7d**) with visible light (λ > 400 nm) recorded in CD_2Cl_2 at 23 °C.

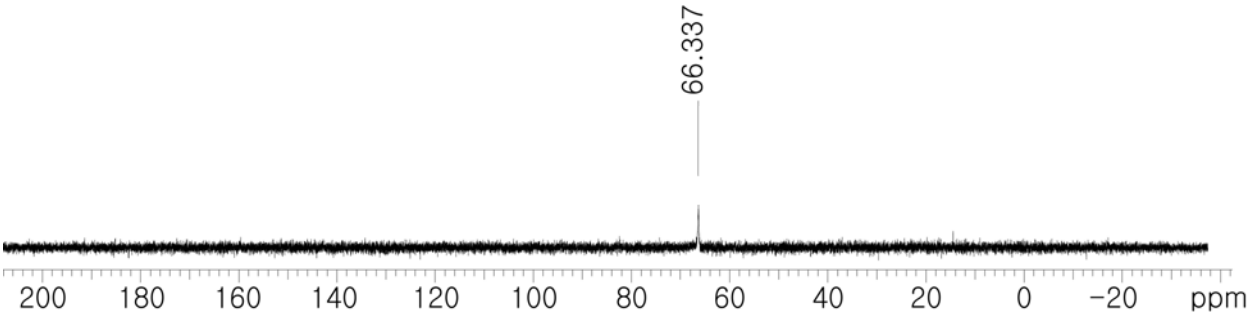

Figure S28. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution obtained by photolysis of $NiBr_3$(dppe) (**7e**) with visible light (λ > 400 nm) recorded in CD_2Cl_2 at 23 °C.

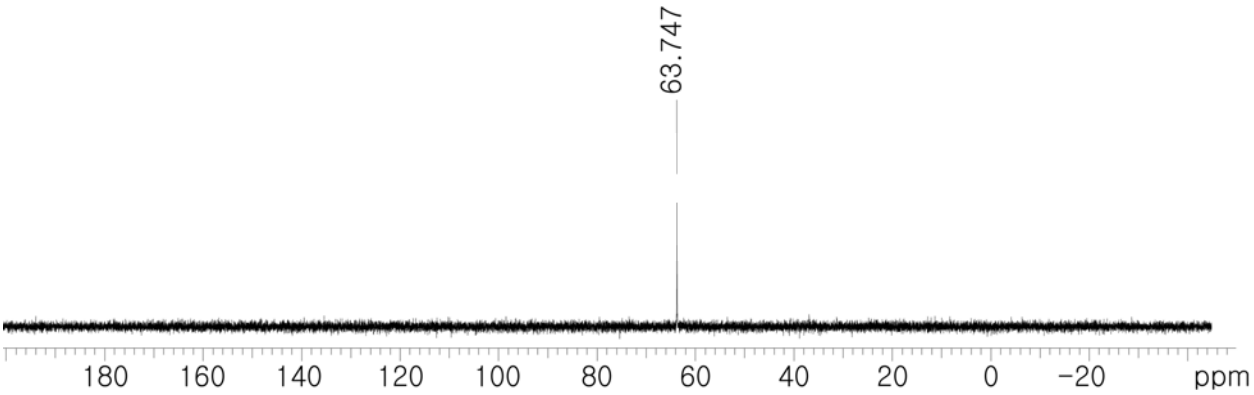

Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution obtained by photolysis of $NiBr_3$(dppe-OMe) (**7e-OMe**) with visible light (λ > 400 nm) recorded in CD_2Cl_2 at 23 °C.

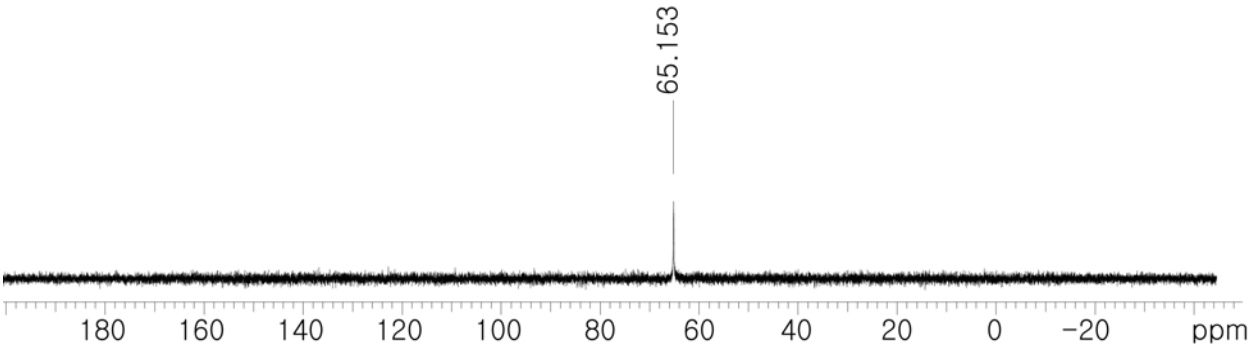

Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution obtained by photolysis of $NiBr_3$(dppe-Cl) (**7e-Cl**) with visible light (λ > 400 nm) recorded in CD_2Cl_2 at 23 °C.

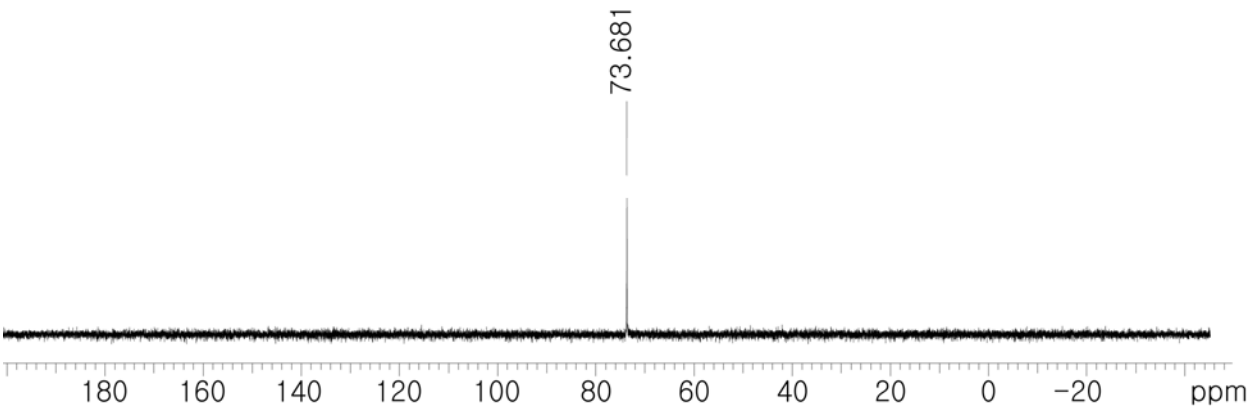

Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution obtained by photolysis of $NiBr_3$(dppey) (**7f**) with visible light (λ > 400 nm) recorded in CD_2Cl_2 at 23 °C.

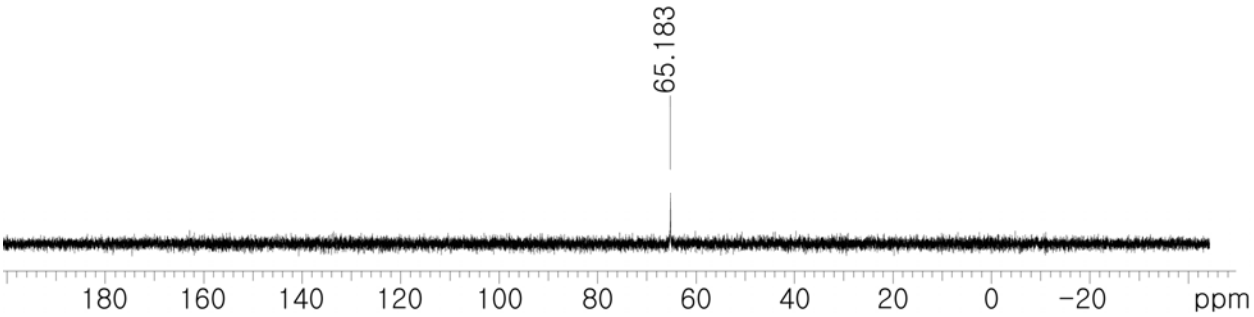

Figure S32. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction solution obtained by photolysis of $NiBr_3$(dppb) (**7g**) with visible light (λ > 400 nm) recorded in CD_2Cl_2 at 23 °C.

F. Nanosecond Transient Absorption Spectroscopy

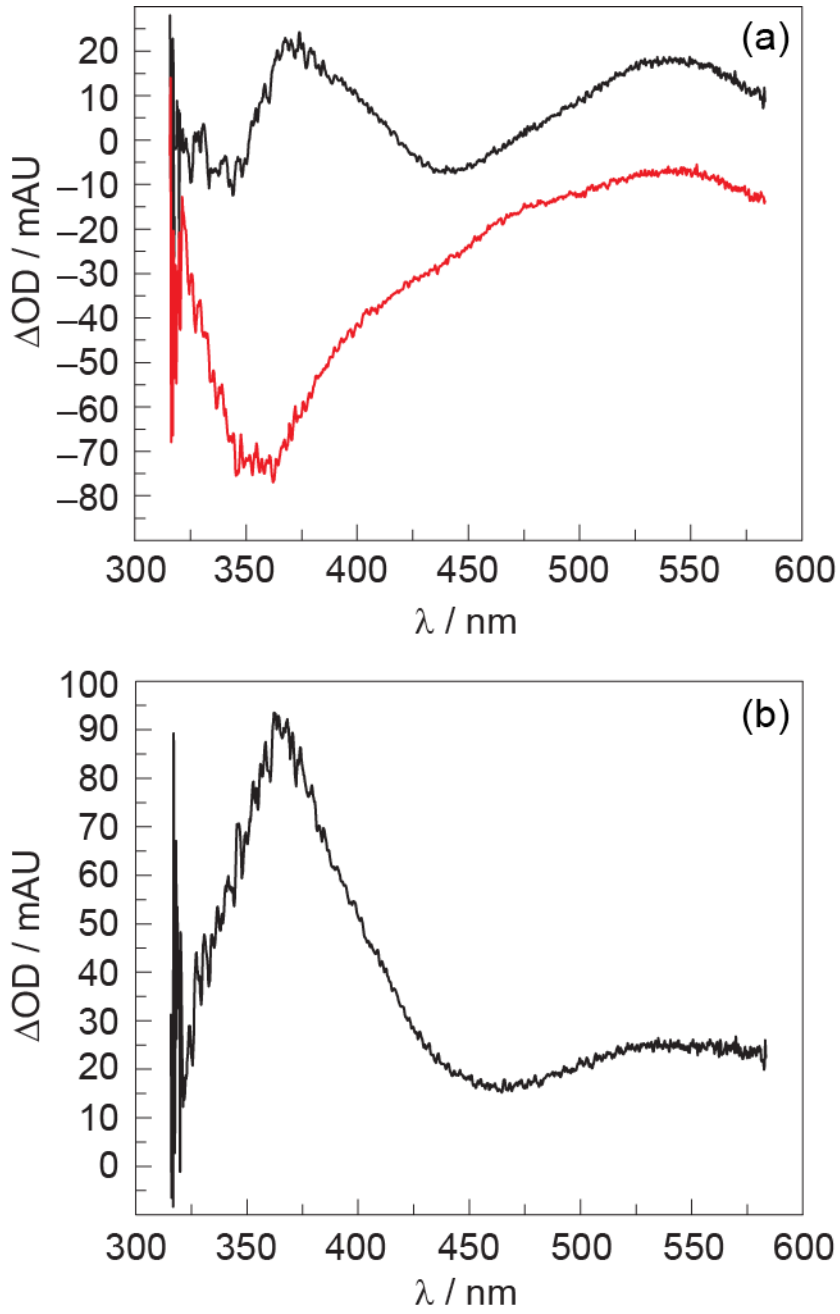

Figure S33. Transient absorption spectra obtained by laser flash photolysis (355 nm pump) of $NiCl_3$(dppe) (**7a**) (0.44 mM solution in MeCN). (a) Transient absorption spectra recorded at 50 ns (—, black), and 50 μs (—, red) after laser pulse. (b) Absorption spectrum of the intermediate species (**8a**) calculated from the difference of TA spectra recorded at 50 ns and 50 μs.

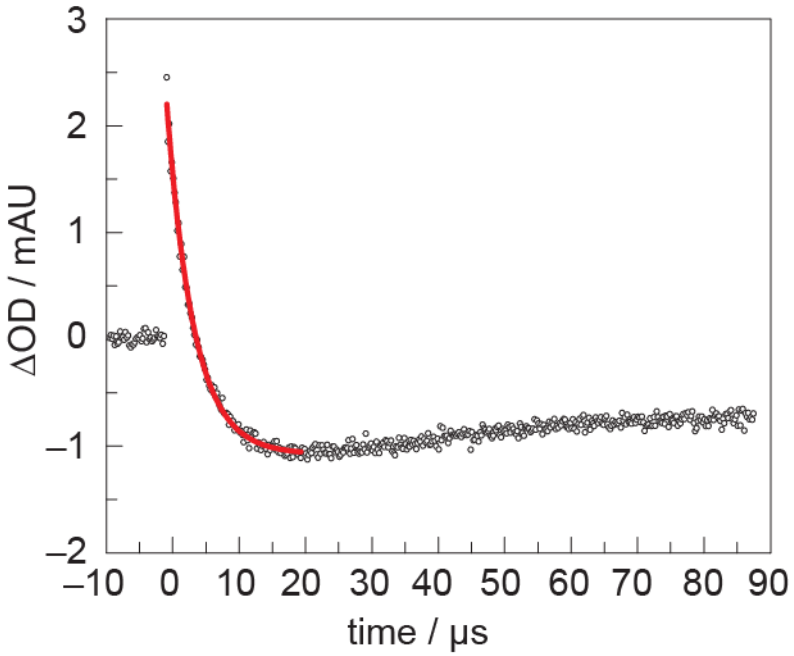

Figure S34. Single wavelength kinetic trace of a MeCN solution of $NiCl_3$(dppe) (**7a**) pumped at 355 nm and recorded at 560 nm. Initial component lifetime: τ = 4.0 ± 0.1 μs.

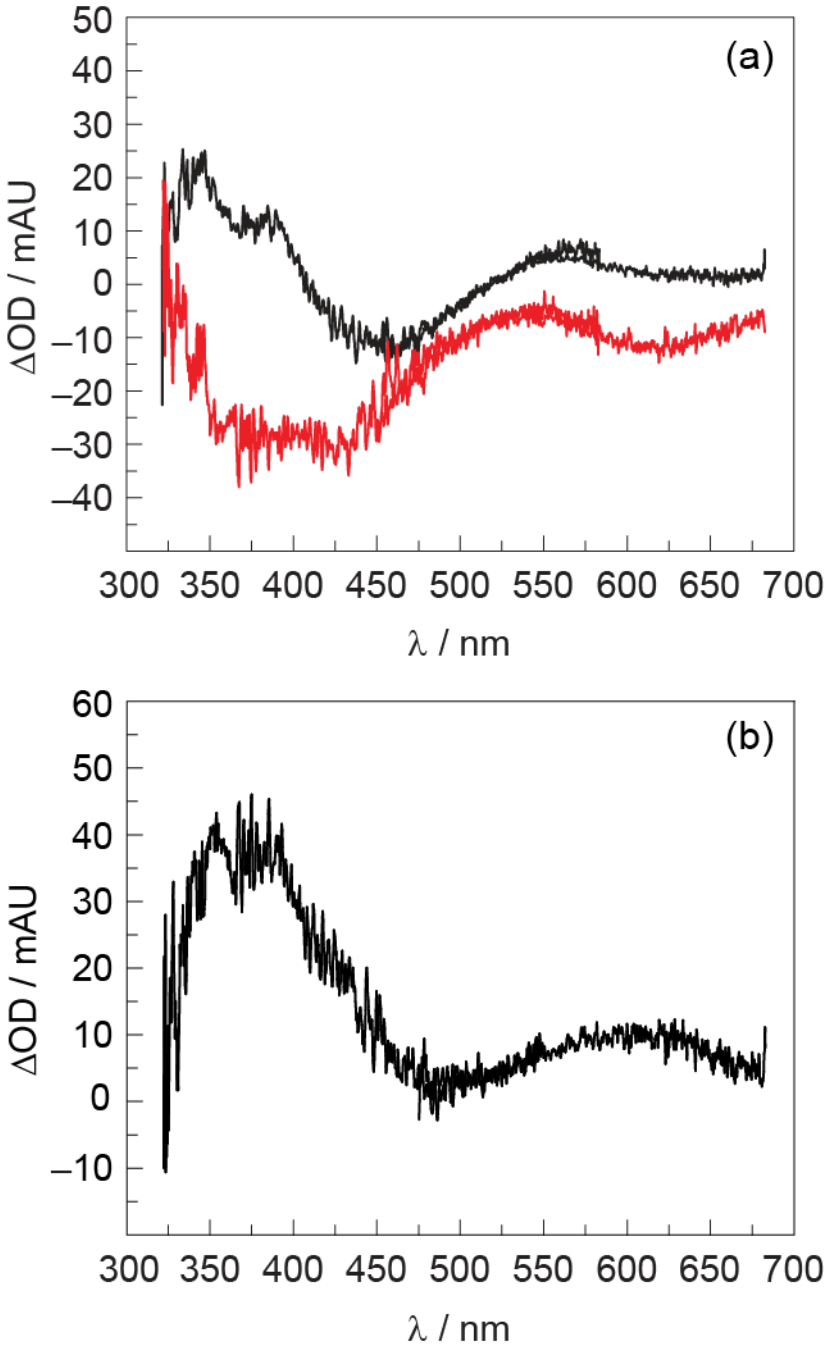

Figure S35. Transient absorption spectra obtained by laser flash photolysis (355 nm pump) of $NiCl_3$(dppe-OMe) (**7a-OMe**) (0.44 mM solution in MeCN). TA spectra are composites of spectra acquired with windows centered at 450 and 550 nm. (a) Transient absorption spectra recorded at 70 ns (—, black), and 50 μs (—, red) after laser pulse. (b) Absorption spectrum of the intermediate species (**8a-OMe**) calculated from the difference of TA spectra recorded at 70 ns and 50 μs.

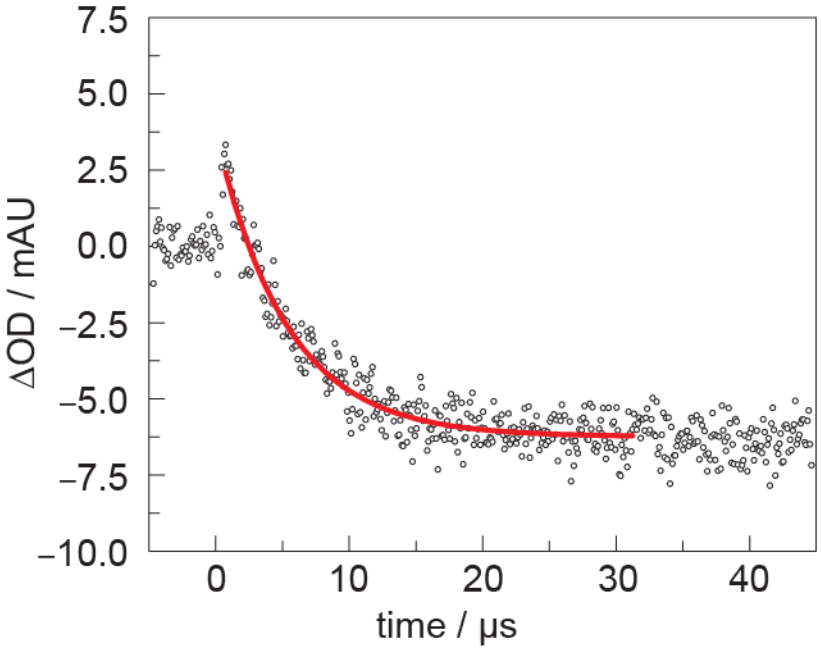

Figure S36. Single wavelength kinetic trace of a MeCN solution of $NiCl_3$(dppe-OMe) (**7a-OMe**) pumped at 355 nm and recorded at 600 nm. Initial component lifetime: τ = 5.3 ± 0.2 µs.

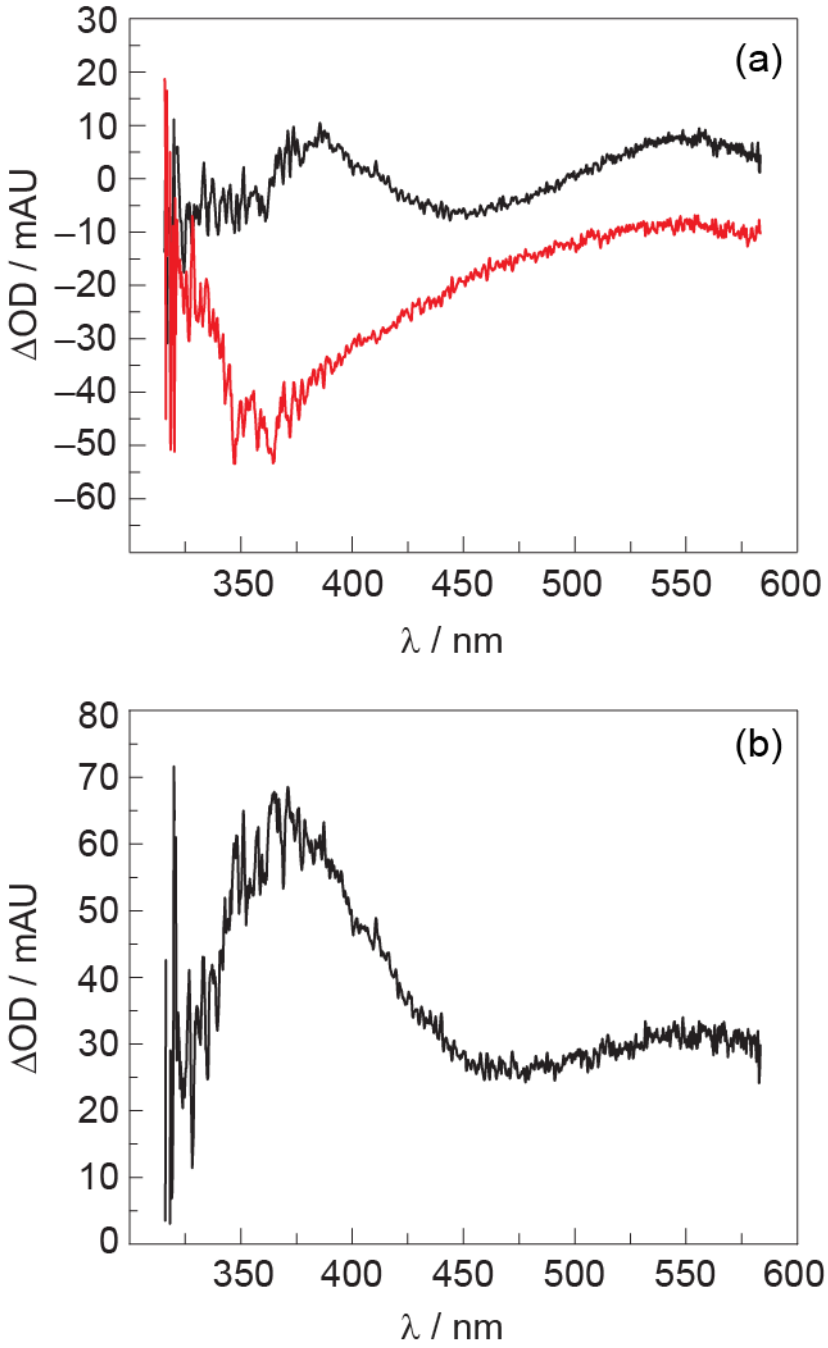

Figure S37. Transient absorption spectra obtained by laser flash photolysis (355 nm pump) of $NiCl_3$(dppe-Cl) (**7a-Cl**) (0.44 mM solution in MeCN). (a) Transient absorption spectra recorded at 70 ns (—, black) and 50 μs (—, red) after laser pulse. (b) Absorption spectrum of the intermediate species (**8a-Cl**) calculated from the difference of TA spectra recorded at 70 ns and 50 μs.

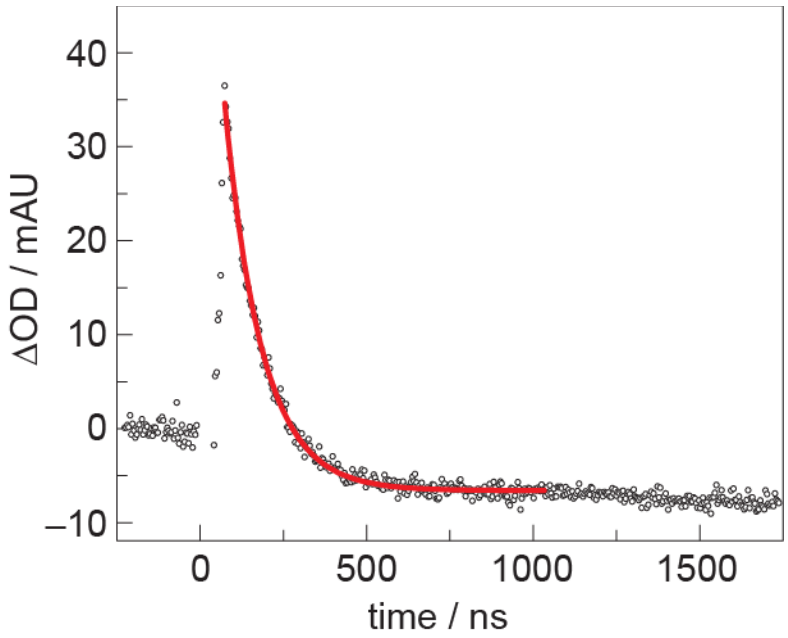

Figure S38. Single wavelength kinetic trace of a MeCN solution of $NiCl_3$(dppe-Cl) (**7a-Cl**) pumped at 355 nm and recorded at 550 nm. Initial component lifetime: τ = 100 ± 1 ns.

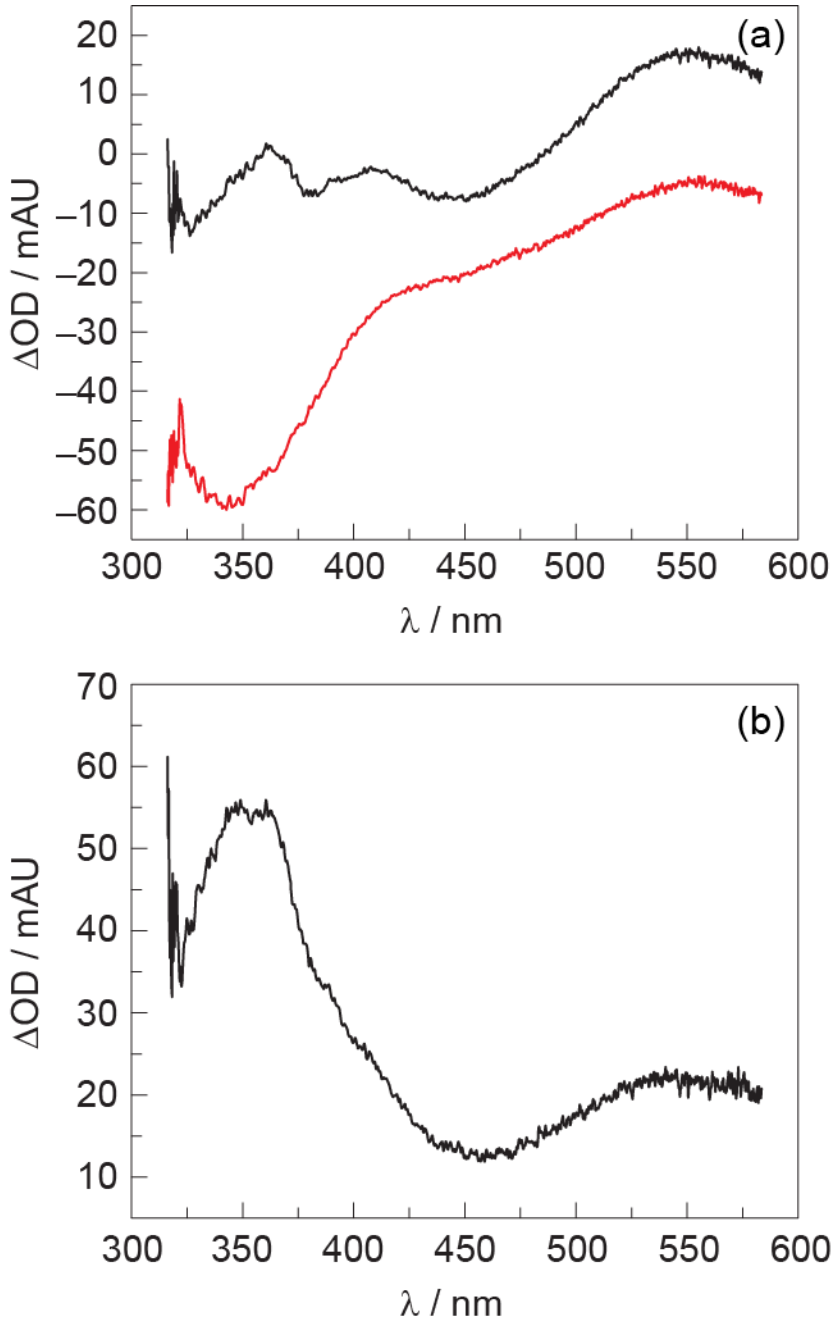

Figure S39. Transient absorption spectra obtained by laser flash photolysis (355 nm pump) of $NiCl_3$(dppey) (**7b**) (0.44 mM solution in MeCN). (a) Transient absorption spectra recorded at 50 ns (—, black), and 50 μs (—, red) after laser pulse. (b) Absorption spectrum of the intermediate species (**8b**) calculated from the difference of TA spectra recorded at 50 ns and 50 μs.

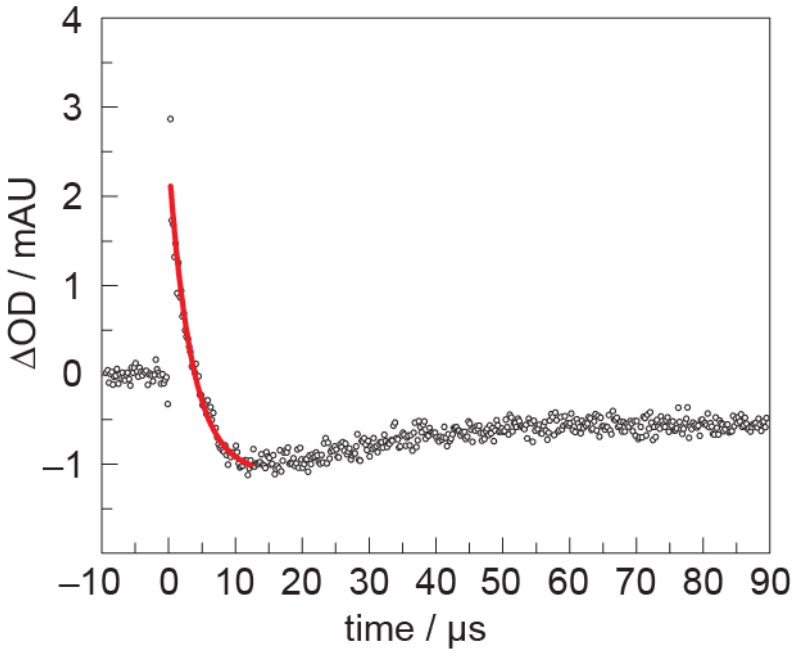

Figure S40. Single wavelength kinetic trace of a MeCN solution of $NiCl_3$(dppey) (**7b**) pumped at 355 nm and recorded at 550 nm. Initial component lifetime: $\tau = 3.4 \pm 0.2$ μs.

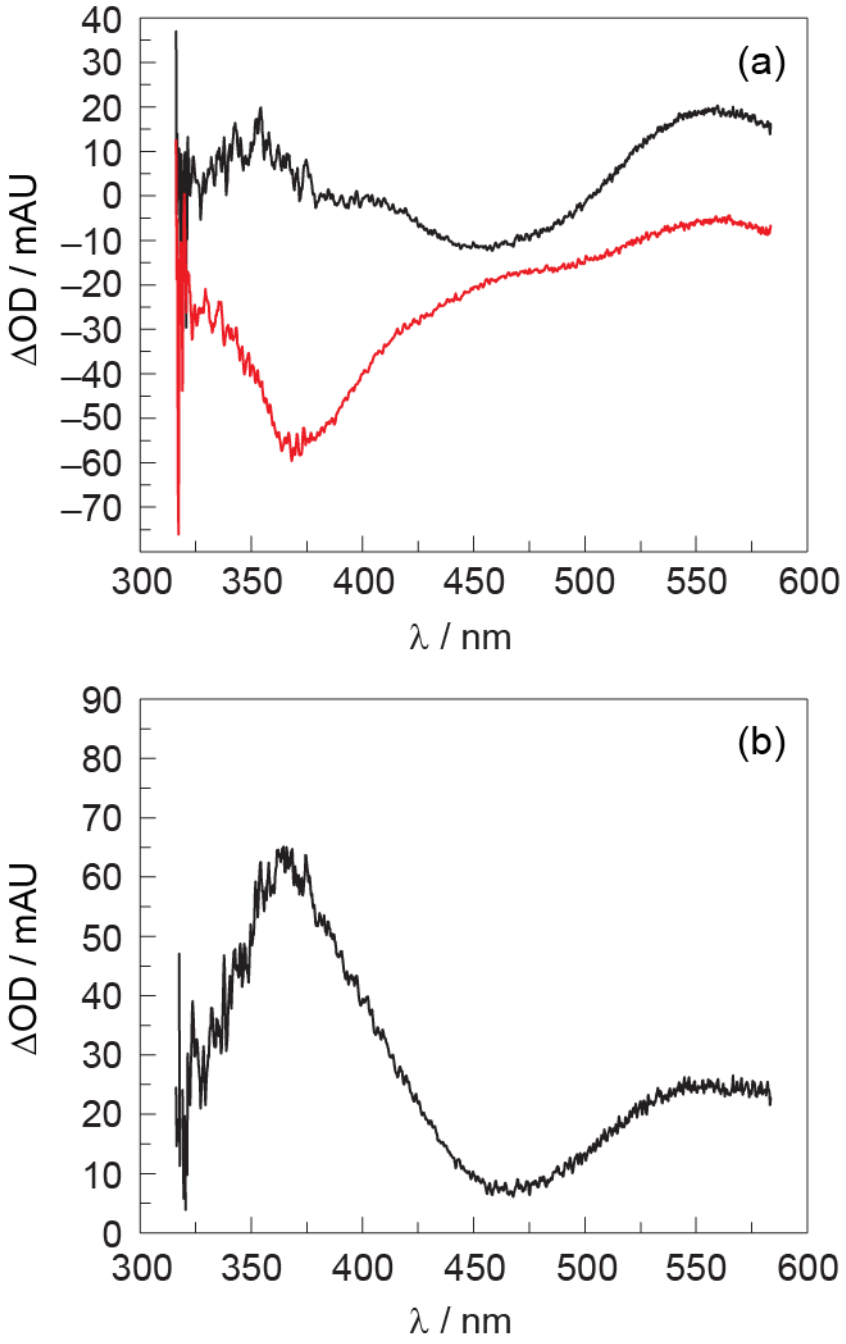

Figure S41. Transient absorption spectra obtained by laser flash photolysis (355 nm pump) of $NiCl_3$(dppb) (**7c**) (0.44 mM solution in MeCN). (a) Transient absorption spectra recorded at 300 ns (—, black), and 50 μs (—, red) after laser pulse. (b) Absorption spectrum of the intermediate species (**8c**) calculated from the difference of TA spectra recorded at 300 ns and 50 μs.

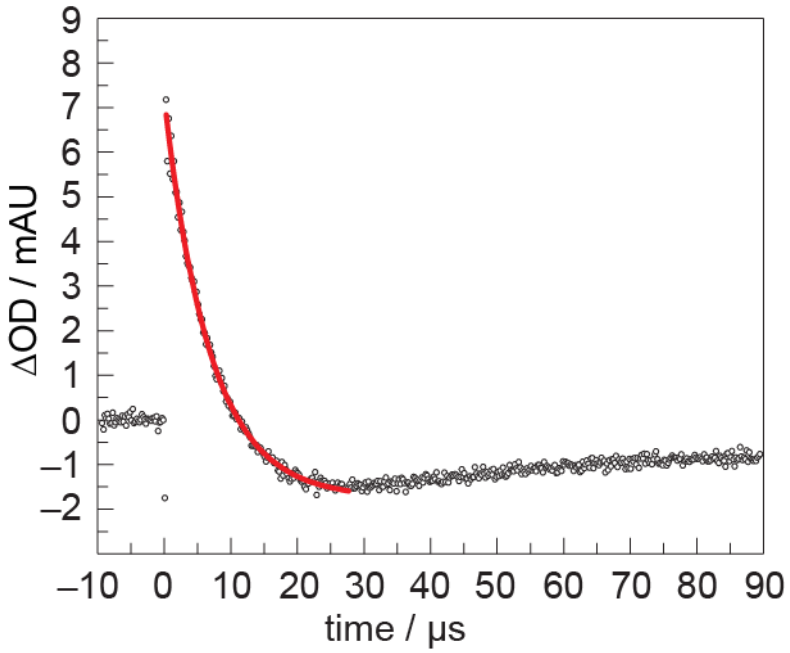

Figure S42. Single wavelength kinetic trace of a MeCN solution of $NiCl_3$(dppb) (**7c**) pumped at 355 nm and recorded at 550 nm. Initial component lifetime: $\tau = 6.8 \pm 0.1$ μs.

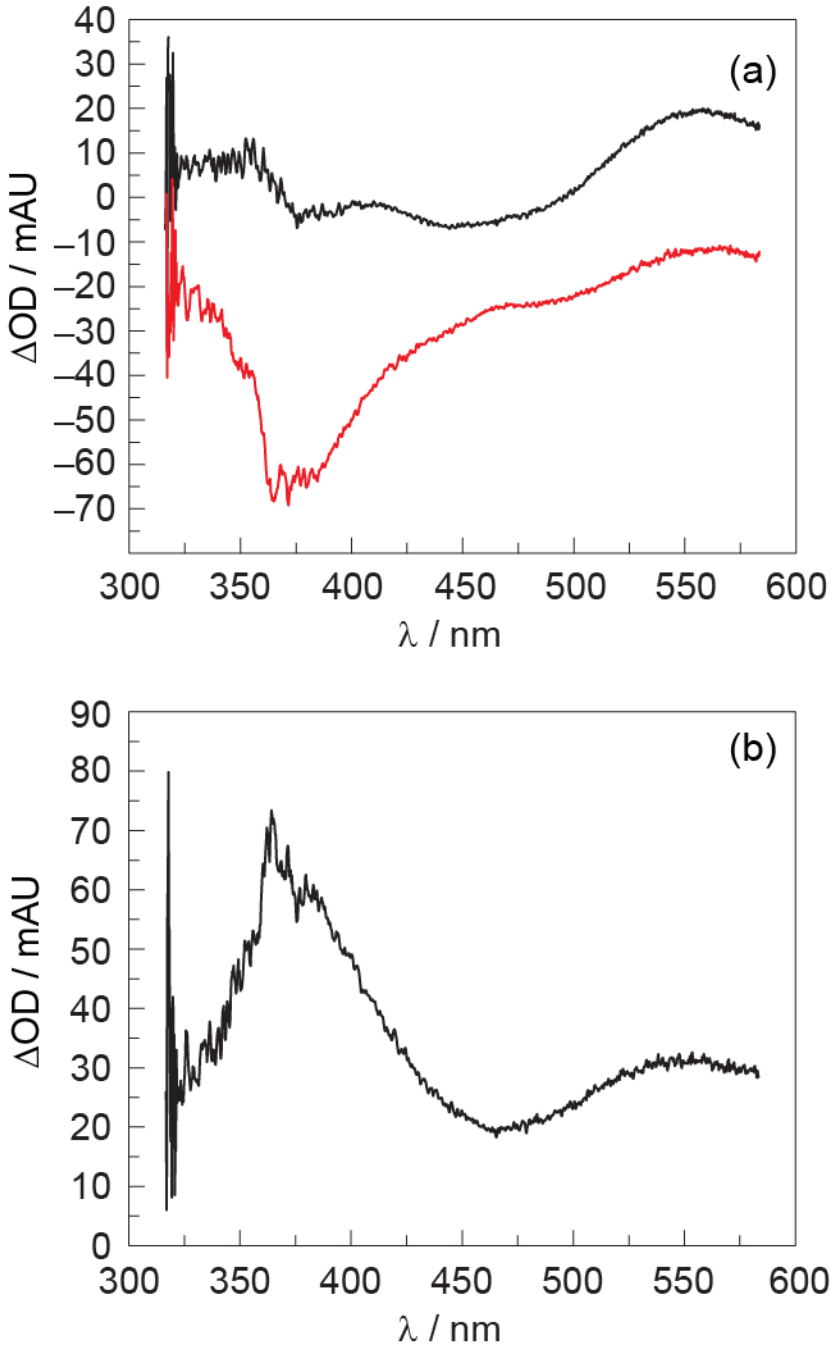

Figure S43. Transient absorption spectra obtained by laser flash photolysis (355 nm pump) of $NiCl_3$(dppb) (**7c**) (0.44 mM solution in 30/70 benzene/MeCN). (a) Transient absorption spectra recorded at 300 ns (—, black), and 50 μs (—, red) after laser pulse. (b) Absorption spectrum of the intermediate species (**8c**) calculated from the difference of TA spectra recorded at 300 ns and 50 μs.

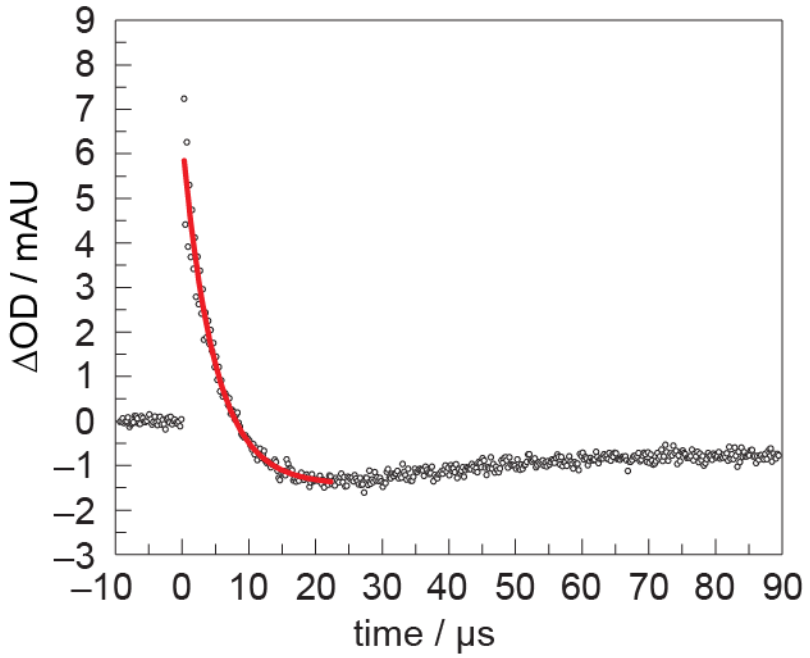

Figure S44. Single wavelength kinetic trace of a solution (0.44 mM in 30:70 benzene:MeCN) of $NiCl_3$(dppb) (**7c**) pumped at 355 nm and recorded at 550 nm. Initial component lifetime: $\tau = 4.7 \pm 0.2$ μs.

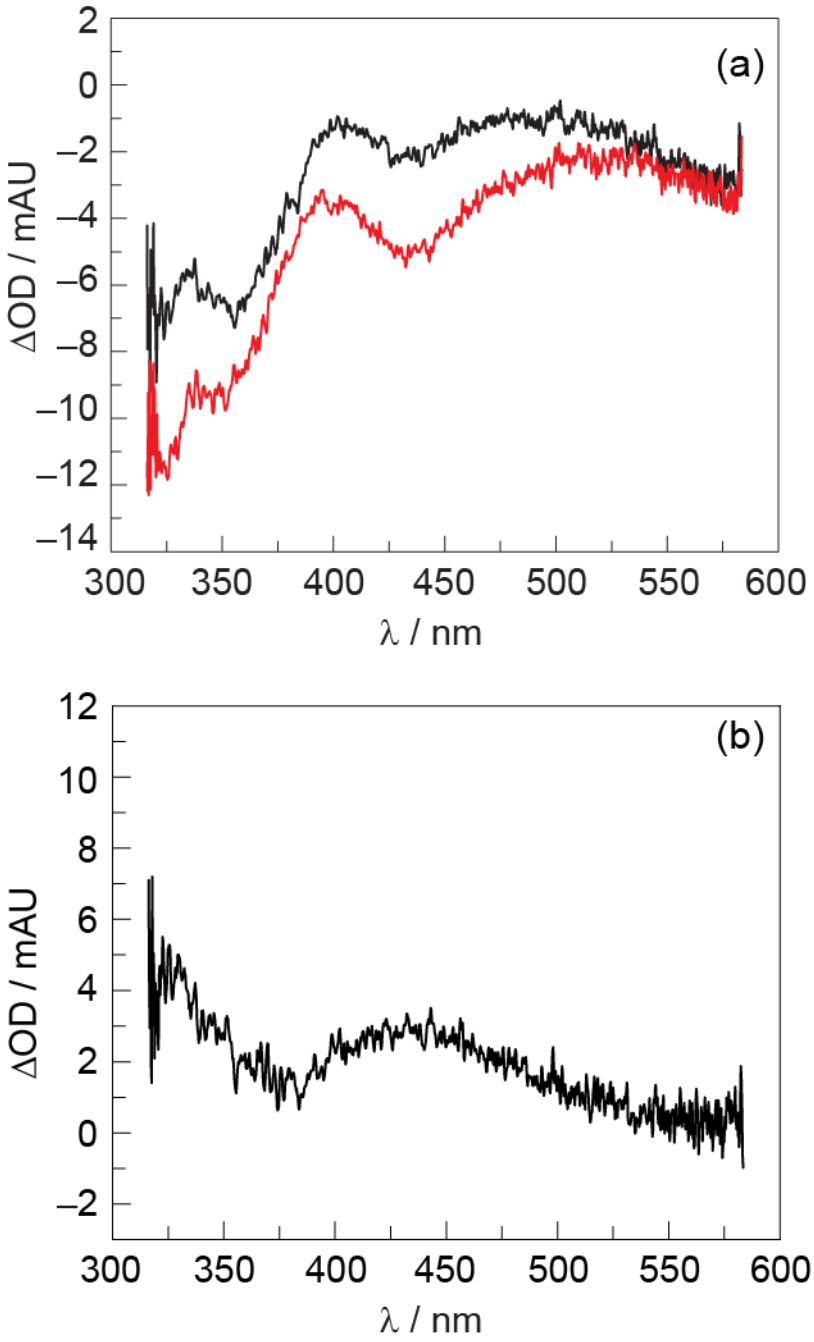

Figure S45.Transient absorption spectra obtained by laser flash photolysis (355 nm pump) of $NiCl_3$(dcpe) (**7d**) (0.44 mM solution in MeCN). (a) Transient absorption spectra recorded at 80 ns (—, black), and 50 μs (—, red) after laser pulse. (b) Absorption spectrum of the intermediate species (**8d**) calculated from the difference of TA spectra recorded at 80 ns and 50 μs.

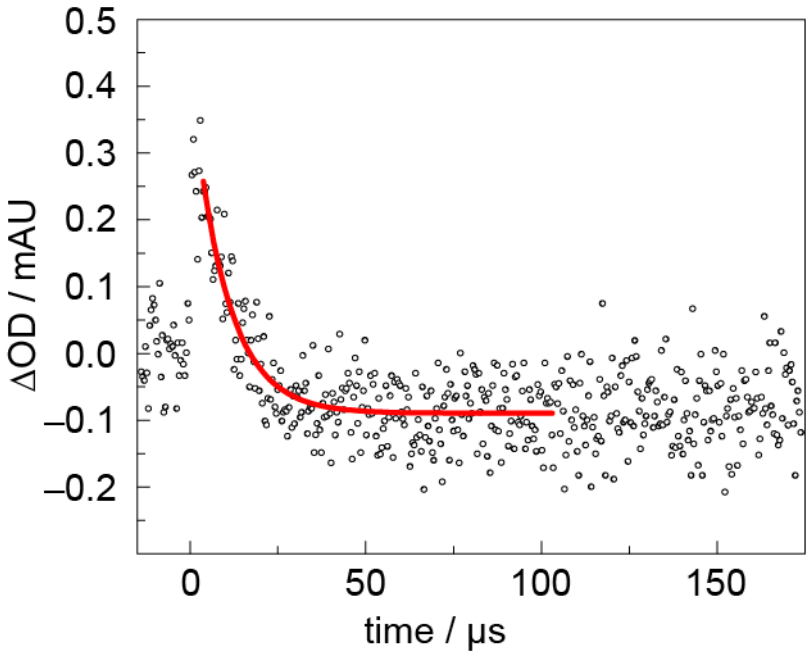

Figure S46. Single wavelength kinetic trace of a solution of $NiCl_3$(dcpe) (**7d**) pumped at 355 nm and recorded at 440 nm. Initial component lifetime: τ = 9.8 ± 0.8 μs.

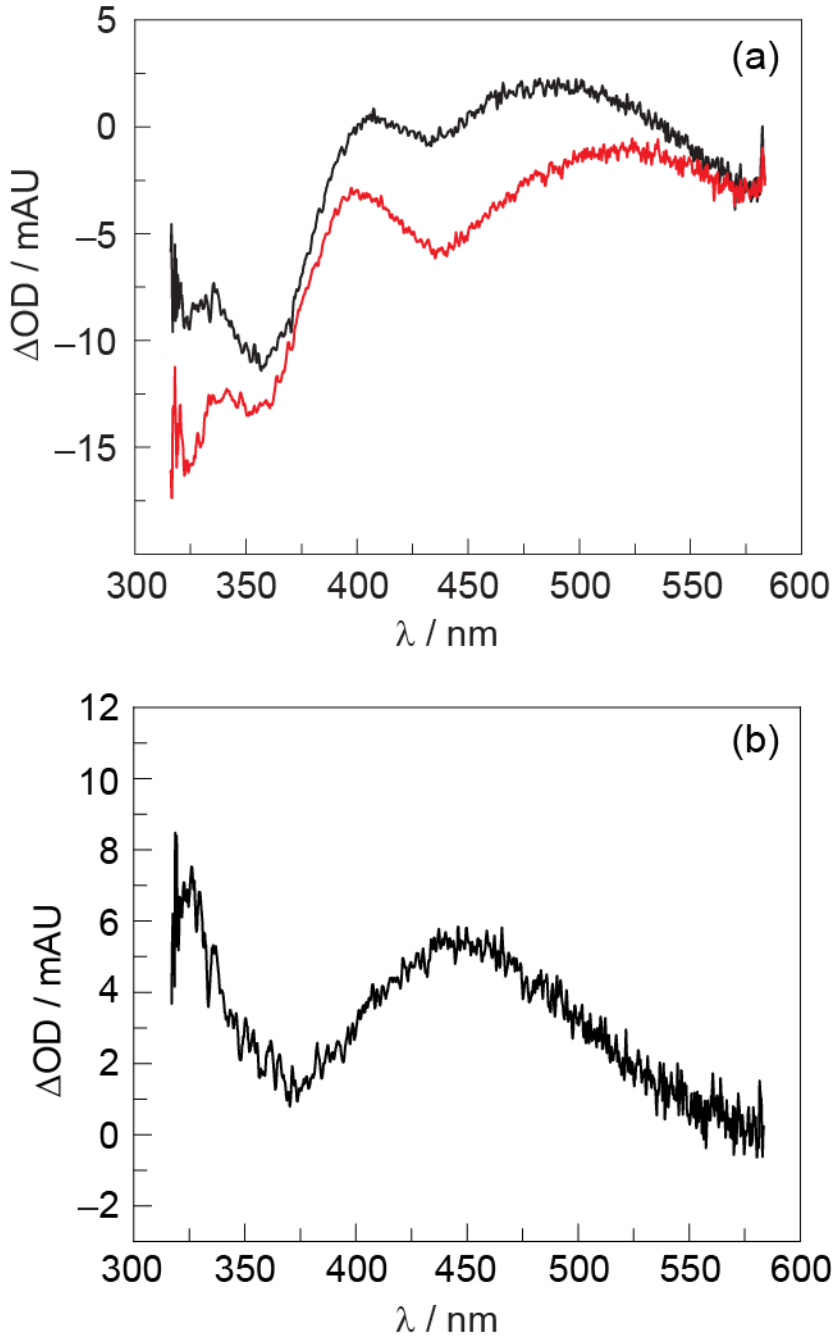

Figure S47. Transient absorption spectra obtained by laser flash photolysis (355 nm pump) of $NiCl_3$(dcpe) (**7d**) (0.44 mM solution in 30:70 benzene:MeCN). (a) Transient absorption spectra recorded at 380 ns (—, black), and 50 μs (—, red) after laser pulse. (b) Absorption spectrum of the intermediate species (**8d**) calculated from the difference of TA spectra recorded at 380 ns and 50 μs.

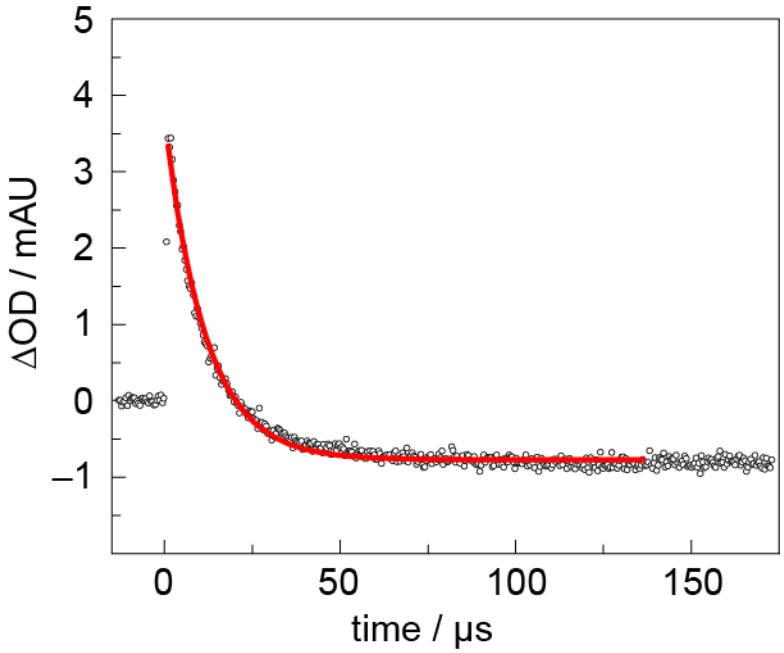

Figure S48. Single wavelength kinetic trace of a solution (0.44 mM in 30:70 benzene:MeCN) $NiCl_3$(dcpe) (**7d**) pumped at 355 nm and recorded at 550 nm. Initial component lifetime: τ = 11.5 ± 0.1 μs.

G. Solution Calorimetry Data

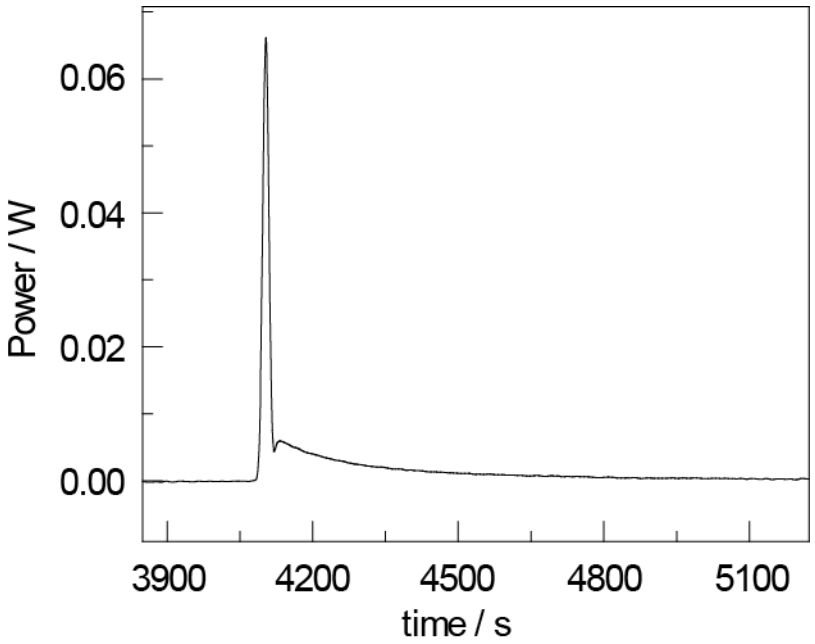

Figure S49. Thermogram for reaction of $NiCl_2$(dppey) (**9b**) with $PhICl_2$ in CH_2Cl_2.

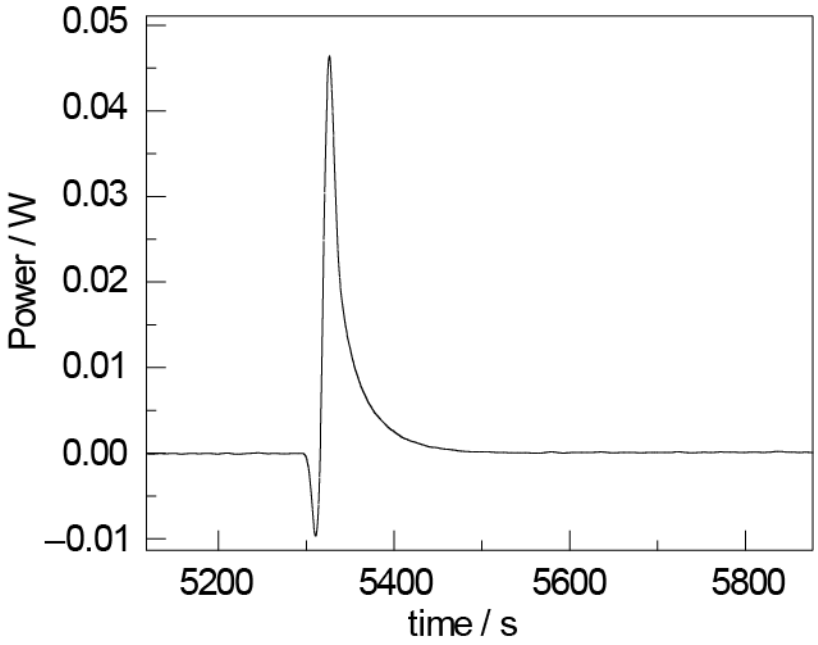

Figure S50. Thermogram for reaction of $NiCl_2$(dppb) (**9c**) with $PhICl_2$ in CH_2Cl_2.

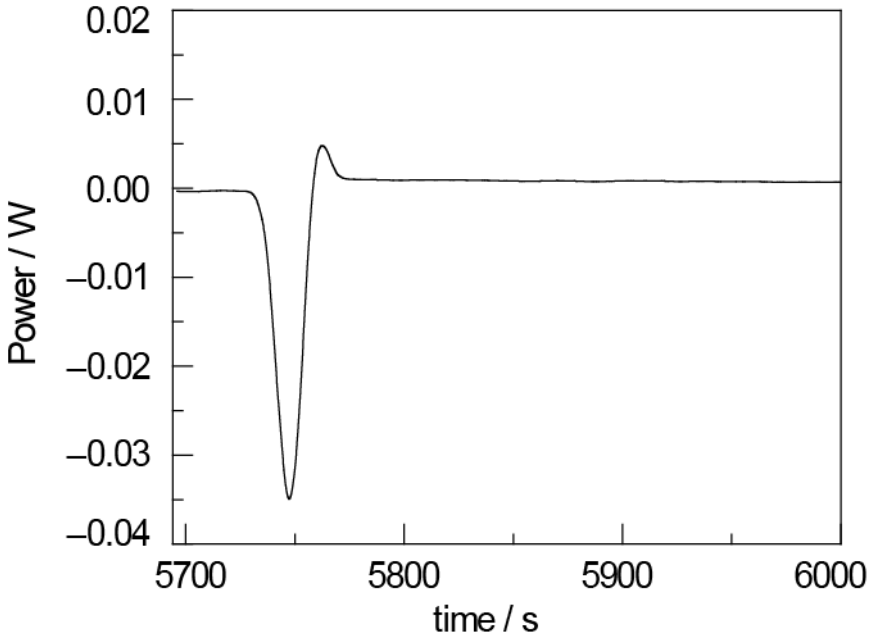

Figure S51. Thermogram for reaction of $NiCl_2$(dcpe) (**9d**) with $PhICl_2$ in CH_2Cl_2.

H. Computational Details

H.1. XYZ Coordinates

Table S6. Cartesian coordinates of the geometry-optimized $NiCl_3$(dppe) (**7a**).

Atom Type	x	y	z
Ni	0.061335	−0.65323	1.135742
Cl	0.135629	−2.851292	0.312622
Cl	−1.610794	−0.732096	2.630764
Cl	1.706671	−0.312504	2.633743
P	−1.523559	−0.08222	−0.41261
P	1.597432	−0.106314	−0.433477
C	−2.903612	−1.256235	−0.675578
C	−2.768036	−2.344123	−1.550349
H	−1.83634	−2.521717	−2.065657
C	−3.823729	−3.234864	−1.729887
H	−3.70682	−4.072643	−2.403344
C	−5.017037	−3.058452	−1.029338
H	−5.832758	−3.755469	−1.164997
C	−5.150657	−1.989925	−0.143051
H	−6.066975	−1.857687	0.415385
C	−4.099985	−1.093414	0.039163
H	−4.206356	−0.280472	0.741031
C	−2.325312	1.560004	−0.170754
C	−3.116054	2.102229	−1.199508
H	−3.285112	1.544405	−2.111074
C	−3.705841	3.354589	−1.048529
H	−4.315257	3.760079	−1.844712
C	−3.51655	4.079685	0.130082
H	−3.97819	5.050641	0.247769
C	−2.741481	3.544452	1.156527
H	−2.602	4.09502	2.076603
C	−2.147102	2.28958	1.010883
H	−1.578421	1.865397	1.82416
C	−0.644164	0.101431	−2.071353
H	−1.247308	−0.345345	−2.862079
H	−0.587293	1.172854	−2.26667
C	0.768661	−0.507756	−2.05211
H	1.362443	−0.145548	−2.892813
H	0.720117	−1.59323	−2.108548

C	1.954349	1.700584	–0.530643
C	2.511394	2.249147	–1.699558
H	2.761516	1.614283	–2.538404
C	2.770686	3.614856	–1.784201
H	3.201369	4.023863	–2.688026
C	2.480996	4.450849	–0.703833
H	2.684045	5.510977	–0.770373
C	1.938672	3.913891	0.461723
H	1.721622	4.553859	1.305618
C	1.675037	2.546323	0.551475
H	1.282852	2.132353	1.468102
C	3.227194	–0.938068	–0.44569
C	4.367257	–0.251601	0.001114
H	4.285793	0.762703	0.360972
C	5.610713	–0.878793	–0.006407
H	6.481313	–0.341979	0.344346
C	5.729662	–2.195541	–0.450923
H	6.695436	–2.682347	–0.45093
C	4.597663	–2.887843	–0.880618
H	4.680124	–3.915069	–1.207783
C	3.349126	–2.269698	–0.874248
H	2.474011	–2.834165	–1.155559

Table S7. Cartesian coordinates of the geometry-optimized $NiCl_3$(dppe-OMe) (**7a-OMe**).

Atom Type	x	y	z
Ni	0.07843	–0.865562	1.026559
Cl	0.017386	–3.048323	0.137741
Cl	–1.594097	–0.867672	2.534611
Cl	1.736065	–0.720538	2.547177
P	–1.488722	–0.212545	–0.505056
P	1.616644	–0.232754	–0.526647
C	–2.959628	–1.266766	–0.727037
C	–2.935474	–2.398828	–1.563225
H	–2.030138	–2.677739	–2.079853
C	–4.056965	–3.198286	–1.70306
H	–4.046972	–4.071096	–2.338802
C	–5.223992	–2.899973	–0.990219
C	–5.259686	–1.793061	–0.138326
H	–6.142789	–1.553665	0.433034
C	–4.12864	–0.990528	–0.006646
H	–4.161434	–0.150514	0.670275
C	–2.140544	1.484956	–0.247835
C	–2.928436	2.09401	–1.247128
H	–3.181605	1.550722	–2.147948
C	–3.40676	3.383337	–1.087536
H	–4.014378	3.856759	–1.844892
C	–3.11099	4.098336	0.080959
C	–2.342475	3.508653	1.084916
H	–2.110433	4.036561	1.996606
C	–1.863749	2.207942	0.915566
H	–1.295803	1.751248	1.711715
C	–0.633213	–0.117354	–2.18644
H	–1.226923	–0.651498	–2.928156
H	–0.628931	0.936194	–2.465671
C	0.803836	–0.66602	–2.141252
H	1.394512	–0.31565	–2.989758
H	0.797223	–1.755206	–2.163765
C	1.871213	1.584815	–0.546345
C	1.99401	2.302022	–1.744331
H	1.934904	1.797758	–2.698462
C	2.201386	3.681748	–1.747082

H	2.288731	4.200762	–2.689311
C	2.296295	4.364754	–0.531945
C	2.185824	3.663117	0.673181
H	2.269085	4.210332	1.600681
C	1.972524	2.294353	0.668343
H	1.900777	1.762529	1.606708
C	3.269663	–1.006663	–0.56001
C	4.443263	–0.229495	–0.555127
H	4.385826	0.847819	–0.525174
C	5.690547	–0.833044	–0.585615
H	6.597202	–0.246185	–0.580364
C	5.794139	–2.227608	–0.603484
C	4.63864	–3.014378	–0.594345
H	4.69406	–4.091872	–0.590983
C	3.387358	–2.4049	–0.567882
H	2.501506	–3.022502	–0.520078
O	7.086464	–2.732951	–0.627133
O	–6.29166	–3.760695	–1.202578
O	–3.635192	5.381897	0.144121
O	2.497984	5.731649	–0.416286
C	–7.520946	–3.562479	–0.45302
H	–7.973421	–2.596126	–0.683354
H	–8.18248	–4.359497	–0.774883
H	–7.344434	–3.64309	0.620882
C	–3.407855	6.177148	1.340034
H	–3.933457	7.109649	1.16528
H	–3.816316	5.685713	2.224485
H	–2.344412	6.376328	1.484055
C	2.617369	6.533994	–1.62218
H	1.71873	6.459424	–2.237021
H	2.737201	7.55409	–1.274073
H	3.492705	6.241756	–2.205373
C	7.284775	–4.171508	–0.556615
H	8.360465	–4.310004	–0.543104
H	6.849766	–4.584604	0.354668
H	6.862166	–4.671598	–1.429988

Table S8. Cartesian coordinates of the geometry-optimized $NiCl_3$(dppe-Cl) (**7a-Cl**).

Atom Type	x	y	z
Ni	0.061513	–0.646215	1.12516
Cl	0.134545	–2.837524	0.289071
Cl	–1.608913	–0.729511	2.616504
Cl	1.704388	–0.293712	2.617731
P	–1.52315	–0.081391	–0.419551
P	1.595897	–0.101366	–0.44125
C	–2.901101	–1.257518	–0.675541
C	–2.765886	–2.350917	–1.543056
H	–1.837445	–2.533258	–2.061826
C	–3.815863	–3.248549	–1.720841
H	–3.7112	–4.091485	–2.386265
C	–4.992129	–3.050507	–1.012285
C	–5.148932	–1.993371	–0.128145
H	–6.067256	–1.871627	0.425152
C	–4.09569	–1.097643	0.042516
H	–4.207385	–0.284785	0.743327
C	–2.330291	1.556966	–0.175123
C	–3.111928	2.108711	–1.205269
H	–3.275026	1.563673	–2.125204
C	–3.706365	3.359059	–1.056192
H	–4.308907	3.781231	–1.845921
C	–3.514478	4.05221	0.132458
C	–2.759258	3.531975	1.171135
H	–2.637221	4.082985	2.091033
C	–2.166342	2.277835	1.014123
H	–1.608361	1.850258	1.833081
C	–0.647504	0.10452	–2.080321
H	–1.247701	–0.346547	–2.870876
H	–0.597508	1.175896	–2.278118
C	0.769796	–0.495975	–2.063398
H	1.360044	–0.125505	–2.902892
H	0.727443	–1.581197	–2.127493
C	1.962182	1.703356	–0.534303
C	2.519968	2.254489	–1.701218
H	2.769704	1.625841	–2.544391
C	2.78483	3.618747	–1.790185

H	3.215289	4.039517	–2.686071
C	2.489549	4.429675	–0.701644
C	1.951112	3.917621	0.468189
H	1.741898	4.565365	1.30559
C	1.687273	2.549561	0.54883
H	1.297428	2.139305	1.46816
C	3.222225	–0.937497	–0.448394
C	4.363629	–0.256803	0.002956
H	4.290401	0.757668	0.363352
C	5.607992	–0.881915	0.003627
H	6.484756	–0.359078	0.353334
C	5.698305	–2.192485	–0.442353
C	4.585951	–2.899594	–0.874756
H	4.678531	–3.925421	–1.196407
C	3.342812	–2.270939	–0.87115
H	2.469927	–2.837304	–1.15495
Cl	7.32541	–3.012366	–0.449294
Cl	–6.369439	–4.221149	–1.244675
Cl	–4.290728	5.688399	0.331442
Cl	2.831489	6.214302	–0.816258

Table S9. Cartesian coordinates of the geometry-optimized $NiCl_3$(dppey) (**7b**).

Atom Type	x	y	z
Ni	–0.350287	0.810415	–0.000002
Cl	–0.242371	2.298572	1.676987
Cl	–0.242343	2.298572	–1.676989
Cl	–2.538764	–0.013384	–0.000005
P	0.184386	–0.739266	1.562241
P	0.184386	–0.739268	–1.562241
C	0.204021	–2.347097	0.666437
H	0.266615	–3.267959	1.236786
C	–0.916095	–0.983533	2.998543
C	–2.029309	–1.831589	2.904476
H	–2.264405	–2.318527	1.970154
C	–2.863012	–2.011038	4.005988
H	–3.721215	–2.663707	3.925372
C	–2.604051	–1.336206	5.199217
H	–3.258068	–1.471022	6.049972
C	–1.508912	–0.476569	5.290145
H	–1.314476	0.061195	6.207716
C	–0.666545	–0.295999	4.195632
H	0.169183	0.383544	4.268113
C	1.889751	–0.643611	2.257786
C	2.381348	–1.696988	3.048662
H	1.748514	–2.539007	3.294477
C	3.682514	–1.656535	3.542644
H	4.050107	–2.470533	4.152453
C	4.506967	–0.56652	3.255593
H	5.516468	–0.53532	3.642241
C	4.022835	0.484276	2.479208
H	4.651963	1.337149	2.265239
C	2.720218	0.448998	1.979565
H	2.339862	1.283269	1.410345
C	0.204021	–2.347097	–0.666436
H	0.266615	–3.267961	–1.236783
C	–0.916096	–0.983534	–2.998543
C	–2.029303	–1.831599	–2.904479
H	–2.264395	–2.318544	–1.970161
C	–2.863007	–2.011047	–4.005992

H	–3.721206	–2.663722	–3.925379
C	–2.604052	–1.336206	–5.199216
H	–3.258069	–1.471021	–6.049971
C	–1.50892	–0.47656	–5.29014
H	–1.314489	0.061211	–6.207709
C	–0.666552	–0.295991	–4.195628
H	0.169171	0.383558	–4.268106
C	1.889752	–0.643621	–2.257788
C	2.381335	–1.69699	–3.048682
H	1.74849	–2.538996	–3.294512
C	3.682502	–1.656546	–3.542662
H	4.050084	–2.470538	–4.152486
C	4.506969	–0.566547	–3.255592
H	5.516471	–0.535354	–3.642239
C	4.022851	0.484242	–2.479189
H	4.65199	1.337103	–2.265204
C	2.720233	0.448972	–1.979547
H	2.339888	1.283238	–1.410312

Table S10. Cartesian coordinates of the geometry-optimized $NiCl_3$(dppb) (**7c**).

Atom Type	x	y	z
Ni	–0.000033	–0.75484	–0.923544
Cl	–0.000083	–2.669994	0.441758
Cl	–1.668467	–1.105164	–2.385414
Cl	1.668376	–1.105224	–2.385428
P	1.533993	0.271792	0.411835
P	–1.534018	0.271823	0.411844
C	3.179402	–0.485176	0.717005
C	4.349775	0.275263	0.569234
H	4.298502	1.305755	0.25322
C	5.594989	–0.298904	0.823373
H	6.49025	0.29563	0.702254
C	5.685023	–1.631817	1.220769
H	6.652398	–2.076853	1.410489
C	4.523631	–2.39241	1.363069
H	4.586011	–3.430829	1.657751
C	3.274968	–1.829663	1.111035
H	2.381636	–2.430209	1.194119
C	1.873946	2.006056	–0.120134
C	2.120809	2.274874	–1.476976
H	2.095455	1.470621	–2.198257
C	2.406032	3.574878	–1.891219
H	2.594431	3.768551	–2.938203
C	2.442885	4.618576	–0.966679
H	2.664065	5.625711	–1.293155
C	2.192099	4.359622	0.380593
H	2.21634	5.164452	1.102802
C	1.905845	3.062542	0.803933
H	1.7098	2.879232	1.850173
C	0.704175	0.415435	2.055034
C	1.398435	0.496455	3.264889
H	2.478873	0.468535	3.271455
C	0.696709	0.578283	4.469519
H	1.239624	0.624616	5.403467
C	–3.179419	–0.485157	0.717018
C	–4.349813	0.27524	0.569205
H	–4.29857	1.305725	0.253165

C	–5.595012	–0.298962	0.823341
H	–6.49029	0.295539	0.702193
C	–5.685008	–1.631866	1.220773
H	–6.65237	–2.07693	1.41049
C	–4.523594	–2.39242	1.363109
H	–4.585944	–3.430833	1.657814
C	–3.274946	–1.829638	1.111077
H	–2.381595	–2.430155	1.19418
C	–1.873951	2.006093	–0.120121
C	–2.120766	2.274924	–1.476969
H	–2.09539	1.470677	–2.198256
C	–2.405972	3.574932	–1.89121
H	–2.594335	3.768614	–2.938199
C	–2.442853	4.618622	–0.966662
H	–2.664019	5.62576	–1.293137
C	–2.192112	4.359655	0.380616
H	–2.216373	5.16448	1.10283
C	–1.905875	3.062572	0.803954
H	–1.709863	2.879252	1.850198
C	–0.704187	0.415445	2.055039
C	–1.398437	0.496473	3.2649
H	–2.478876	0.468569	3.271475
C	–0.696701	0.578291	4.469524
H	–1.239608	0.624633	5.403477

Table S11. Cartesian coordinates of the geometry-optimized $NiCl_3$(dcpe) (**7d**).

Atom Type	x	y	z
Ni	–0.066209	0.04096	1.179332
Cl	0.159949	–2.23898	1.655634
Cl	1.454366	1.18143	2.41639
Cl	–1.791801	0.424849	2.572541
P	1.573426	–0.08126	–0.421207
P	–1.672252	–0.095857	–0.480926
C	2.485858	1.48133	–0.960304
C	1.558256	2.732121	–0.978265
H	0.887255	2.70383	–0.121085
C	2.357598	4.059071	–0.932361
H	2.535112	4.341182	0.108186
C	3.703792	3.928229	–1.657737
H	4.211553	4.893902	–1.700203
C	4.60313	2.882822	–0.94986
H	5.259634	3.382517	–0.233435
C	3.786096	1.804523	–0.189964
H	4.403876	0.919066	–0.063583
C	2.812214	–1.467652	–0.181103
C	3.781254	–1.634011	–1.393635
H	4.108824	–0.668953	–1.784827
C	5.030819	–2.465406	–1.002576
H	5.801684	–1.804019	–0.597184
C	4.686103	–3.535897	0.044486
H	5.551394	–4.176165	0.228996
C	4.207376	–2.886335	1.370243
H	5.04774	–2.789069	2.062068
C	3.578071	–1.48569	1.160983
H	4.355168	–0.721537	1.165754
C	0.676916	–0.628398	–1.980517
H	1.278703	–0.380511	–2.858334
H	0.618906	–1.71626	–1.923746
C	–0.736887	–0.031547	–2.107302
H	–1.305367	–0.55584	–2.879804
H	–0.682361	1.01618	–2.407836
C	–2.741783	–1.642819	–0.551606
C	–3.979048	–1.524456	–1.479061

H	–3.648403	–1.616708	–2.517936
C	–4.990266	–2.65571	–1.145675
H	–5.591371	–2.860717	–2.035775
C	–4.289035	–3.950634	–0.670726
H	–4.915263	–4.817745	–0.890632
C	–2.916231	–4.093166	–1.342243
H	–3.056483	–4.123706	–2.427396
C	–1.960211	–2.927592	–0.956568
H	–1.315193	–2.720146	–1.814128
C	–2.846631	1.379423	–0.617214
C	–4.122736	1.313666	0.295078
H	–4.074354	0.47323	0.98343
C	–4.342614	2.601058	1.109198
H	–3.579089	2.674109	1.884305
C	–4.323771	3.849157	0.211628
H	–4.416487	4.745599	0.828081
C	–3.031428	3.919648	–0.654253
H	–2.476209	4.835082	–0.437645
C	–2.093376	2.71586	–0.426623
H	–1.261848	2.789271	–1.127032
H	–3.293812	3.965768	–1.71571
H	–5.203512	3.832166	–0.438767
H	–5.302398	2.529148	1.626707
H	–4.996936	1.159256	–0.343442
H	–1.670133	2.75406	0.577596
H	–3.17008	1.342774	–1.665615
H	3.526215	2.145319	0.809839
H	5.255474	2.402304	–1.68451
H	1.75619	4.858169	–1.371424
H	0.944149	2.711977	–1.882741
H	3.524803	3.631731	–2.696515
H	2.771281	1.24959	–1.994012
H	3.904778	–4.188736	–0.357343
H	5.455299	–2.921701	–1.900103
H	3.251662	–2.137955	–2.20657
H	2.143064	–2.330662	–0.144719
H	2.905845	–1.25883	1.983546
H	3.475707	–3.53535	1.85475

H	–4.15837	–3.93308	0.414246
H	–2.45108	–5.04117	–1.06516
H	–1.31393	–3.21782	–0.13339
H	–5.68191	–2.30728	–0.37473
H	–4.48325	–0.56707	–1.39378
H	–3.07878	–1.75471	0.482229

Table S12. Cartesian coordinates of the geometry-optimized $NiBr_3$(dppe)(**7e**).

Atom Type	x	y	z
Ni	0.043203	–0.510522	0.81754
Br	0.192606	–2.813368	–0.122706
Br	–1.728172	–0.820077	2.386934
Br	1.73111	–0.150477	2.48262
P	–1.545562	0.198766	–0.697734
P	1.591644	0.14845	–0.712378
C	–2.930785	–0.930929	–1.106648
C	–2.768864	–1.952297	–2.054102
H	–1.817987	–2.1027	–2.542197
C	–3.825056	–2.812439	–2.346202
H	–3.686501	–3.599899	–3.07408
C	–5.047207	–2.670844	–1.689185
H	–5.86343	–3.344249	–1.912563
C	–5.210007	–1.666907	–0.734718
H	–6.150371	–1.560647	–0.211808
C	–4.158267	–0.802569	–0.439019
H	–4.290164	–0.038665	0.311856
C	–2.349297	1.819806	–0.334892
C	–3.09795	2.457893	–1.339911
H	–3.23282	1.98554	–2.303851
C	–3.690082	3.695152	–1.100129
H	–4.266502	4.174127	–1.879881
C	–3.545529	4.310424	0.145337
H	–4.008982	5.269596	0.332129
C	–2.812847	3.680149	1.148691
H	–2.708017	4.144696	2.119481
C	–2.216322	2.439872	0.913603
H	–1.677895	1.944978	1.707807
C	–0.642874	0.525282	–2.323012
H	–1.250274	0.177756	–3.159204
H	–0.552613	1.60864	–2.409019
C	0.751304	–0.122334	–2.354658
H	1.354882	0.292999	–3.163451
H	0.673585	–1.198625	–2.495815
C	1.95752	1.958454	–0.721034
C	2.682129	2.514577	–1.790815

H	3.064025	1.881388	–2.580357
C	2.938928	3.882417	–1.833437
H	3.501204	4.296911	–2.659101
C	2.477975	4.713955	–0.810143
H	2.680114	5.775822	–0.843284
C	1.765674	4.170316	0.256211
H	1.414591	4.806387	1.056748
C	1.506649	2.799391	0.303639
H	0.981732	2.383176	1.149534
C	3.228638	–0.664316	–0.814874
C	4.329043	–0.091864	–0.156306
H	4.206501	0.813526	0.418214
C	5.58126	–0.696507	–0.228487
H	6.419838	–0.249681	0.28742
C	5.750075	–1.877994	–0.951045
H	6.722856	–2.347847	–1.001915
C	4.658673	–2.458898	–1.595792
H	4.778797	–3.383418	–2.143346
C	3.40107	–1.862476	–1.52506
H	2.559391	–2.350088	–1.990478

Table S13. Cartesian coordinates of the geometry-optimized $NiBr_3$(dppe-OMe) (**7e-OMe**).

Atom Type	x	y	z
Ni	0.056179	–0.575813	0.775392
Br	0.118399	–2.881655	–0.184527
Br	–1.696513	–0.82804	2.386744
Br	1.800272	–0.320191	2.406285
P	–1.541274	0.172755	–0.712594
P	1.591278	0.091897	–0.770766
C	–2.95926	–0.913365	–1.093046
C	–2.854546	–1.94844	–2.040779
H	–1.921516	–2.13147	–2.551638
C	–3.932944	–2.7748	–2.309107
H	–3.860335	–3.574737	–3.030772
C	–5.137783	–2.600965	–1.618275
C	–5.254628	–1.591274	–0.659481
H	–6.169052	–1.447873	–0.105356
C	–4.166284	–0.76115	–0.399178
H	–4.263758	0.005028	0.354879
C	–2.280805	1.811092	–0.32829
C	–3.037721	2.483339	–1.31077
H	–3.213315	2.022816	–2.273837
C	–3.583598	3.730625	–1.058973
H	–4.16725	4.250941	–1.804168
C	–3.389717	4.340112	0.188281
C	–2.652524	3.686371	1.176386
H	–2.501073	4.129461	2.148401
C	–2.104982	2.429228	0.912989
H	–1.564227	1.921132	1.697331
C	–0.662492	0.467012	–2.358052
H	–1.285029	0.103633	–3.175965
H	–0.573438	1.548286	–2.465787
C	0.730232	–0.18154	–2.401185
H	1.326112	0.225641	–3.219908
H	0.650424	–1.259065	–2.5348
C	1.939862	1.898663	–0.754637
C	2.557243	2.505215	–1.858989
H	2.862708	1.910681	–2.709511
C	2.815104	3.874435	–1.883728

H	3.29462	4.306026	–2.748693
C	2.454045	4.662137	–0.78512
C	1.84661	4.071372	0.326755
H	1.587921	4.696301	1.168442
C	1.593392	2.707648	0.341143
H	1.150506	2.260839	1.217957
C	3.220432	–0.716841	–0.903411
C	4.36662	–0.095202	–0.369773
H	4.284041	0.861711	0.122497
C	5.607471	–0.702204	–0.45965
H	6.490765	–0.235544	–0.049634
C	5.732753	–1.955498	–1.071006
C	4.604554	–2.59485	–1.591402
H	4.673951	–3.568812	–2.05007
C	3.358297	–1.97849	–1.498011
H	2.491	–2.509616	–1.857843
O	–6.156274	–3.47933	–1.958423
O	–3.976784	5.58726	0.341416
O	2.661567	6.030599	–0.70237
O	7.01633	–2.478446	–1.10941
C	7.2267	–3.802913	–1.669576
H	8.289917	–3.99093	–1.563879
H	6.663447	–4.557461	–1.117734
H	6.952515	–3.833225	–2.726055
C	–7.41845	–3.412854	–1.241846
H	–7.907707	–2.448166	–1.391279
H	–8.029923	–4.200859	–1.66871
H	–7.275452	–3.595735	–0.175347
C	–3.828709	6.289203	1.605983
H	–4.367328	7.222145	1.478163
H	–4.269502	5.720458	2.42673
H	–2.778843	6.497572	1.820208
C	3.309383	6.72125	–1.804688
H	2.722801	6.638902	–2.721831
H	3.360837	7.760513	–1.497986
H	4.31801	6.338569	–1.97216

Table S14. Cartesian coordinates of the geometry-optimized $NiBr_3$(dppe-Cl) (**7e-Cl**).

Atom Type	x	y	z
Ni	0.043697	–0.506619	0.808412
Br	0.190216	–2.800956	–0.14626
Br	–1.724546	–0.816307	2.374903
Br	1.729766	–0.142201	2.46769
P	–1.544265	0.196268	–0.703676
P	1.589934	0.151644	–0.718558
C	–2.930039	–0.933492	–1.106159
C	–2.771097	–1.960259	–2.047814
H	–1.823574	–2.116635	–2.53968
C	–3.823798	–2.824581	–2.33992
H	–3.699548	–3.617002	–3.061718
C	–5.028878	–2.660069	–1.67282
C	–5.212663	–1.667541	–0.721396
H	–6.154911	–1.569499	–0.204779
C	–4.155807	–0.806137	–0.435653
H	–4.291551	–0.042611	0.314582
C	–2.351391	1.814877	–0.340142
C	–3.094205	2.460226	–1.344373
H	–3.227059	1.998577	–2.313359
C	–3.68849	3.697106	–1.10837
H	–4.2609	4.190178	–1.879206
C	–3.53615	4.283584	0.141796
C	–2.820011	3.669765	1.156782
H	–2.728016	4.13782	2.124919
C	–2.226878	2.429771	0.911914
H	–1.696391	1.933299	1.710512
C	–0.645918	0.524313	–2.331587
H	–1.250349	0.171097	–3.167555
H	–0.563621	1.608082	–2.421106
C	0.753779	–0.112915	–2.364515
H	1.353653	0.311552	–3.171214
H	0.683679	–1.188607	–2.513466
C	1.962414	1.960016	–0.72266
C	2.683537	2.520604	–1.791916
H	3.063338	1.895014	–2.588014
C	2.945659	3.887263	–1.837045

H	3.502946	4.314989	–2.656487
C	2.480698	4.691952	–0.804162
C	1.775703	4.171367	0.268971
H	1.43548	4.814265	1.06611
C	1.518669	2.799769	0.306268
H	0.998725	2.385482	1.156156
C	3.225494	–0.662466	–0.817057
C	4.326057	–0.09284	–0.156729
H	4.209695	0.813588	0.417033
C	5.580112	–0.694517	–0.219854
H	6.424521	–0.257902	0.290737
C	5.722413	–1.871198	–0.941397
C	4.652133	–2.469401	–1.589416
H	4.783901	–3.394743	–2.128596
C	3.398522	–1.864738	–1.519654
H	2.560446	–2.356469	–1.986661
Cl	7.36311	–2.658201	–1.032737
Cl	–6.410084	–3.785917	–2.05459
Cl	–4.312161	5.901655	0.454888
Cl	2.818917	6.480239	–0.861923

Table S15. Cartesian coordinates of the geometry-optimized $NiBr_3$(dppey) (**7f**).

Atom Type	x	y	z
Ni	–0.390422	0.881042	0
Br	–2.75102	0.101395	0
Br	–0.300137	2.488148	–1.763222
Br	–0.300136	2.488148	1.763221
P	0.158818	–0.677212	1.5714
P	0.158818	–0.677212	–1.5714
C	0.184975	–2.280056	0.66617
H	0.257891	–3.200946	1.235309
C	–0.91757	–0.968407	3.020827
C	–1.997375	–1.859481	2.935664
H	–2.221585	–2.355691	2.003455
C	–2.81144	–2.077771	4.045126
H	–3.64457	–2.762734	3.969535
C	–2.564896	–1.401408	5.239815
H	–3.203473	–1.566397	6.096942
C	–1.500593	–0.503232	5.324669
H	–1.313898	0.033386	6.244527
C	–0.678931	–0.283121	4.221666
H	0.133867	0.423823	4.29145
C	1.872338	–0.598636	2.256192
C	2.346903	–1.646607	3.064644
H	1.696402	–2.467629	3.333828
C	3.653277	–1.627157	3.545964
H	4.006813	–2.436812	4.169729
C	4.500833	–0.563604	3.228802
H	5.514267	–0.548293	3.605977
C	4.03453	0.481681	2.434342
H	4.681616	1.314651	2.196778
C	2.726729	0.466548	1.947517
H	2.363073	1.297327	1.362569
C	0.184975	–2.280056	–0.66617
H	0.257891	–3.200946	–1.23531
C	–0.91757	–0.968407	–3.020827
C	–1.997375	–1.859481	–2.935664
H	–2.221586	–2.355691	–2.003455
C	–2.81144	–2.077771	–4.045126

H	–3.64457	–2.762734	–3.969535
C	–2.564897	–1.401408	–5.239815
H	–3.203474	–1.566397	–6.096942
C	–1.500593	–0.503232	–5.324669
H	–1.313898	0.033385	–6.244528
C	–0.678931	–0.283121	–4.221666
H	0.133867	0.423822	–4.291451
C	1.872338	–0.598636	–2.256193
C	2.346904	–1.646607	–3.064643
H	1.696403	–2.467629	–3.333827
C	3.653278	–1.627156	–3.545963
H	4.006814	–2.436812	–4.169728
C	4.500833	–0.563603	–3.228802
H	5.514267	–0.548292	–3.605977
C	4.034529	0.481683	–2.434342
H	4.681615	1.314653	–2.196779
C	2.726728	0.466549	–1.947517
H	2.363072	1.297328	–1.36257

Table S16. Cartesian coordinates of the geometry-optimized $NiBr_3$(dppb) (**7g**).

Atom Type	x	y	z
Ni	0.000012	−0.78015	−0.95512
Br	0.000034	−2.8636	0.428741
Br	−1.75859	−1.16821	−2.52768
Br	1.758619	−1.16819	−2.52768
P	1.534471	0.252698	0.392722
P	−1.53446	0.252686	0.392721
C	3.187049	−0.48474	0.706046
C	4.353874	0.187703	0.312488
H	4.293105	1.143926	−0.18368
C	5.604407	−0.38028	0.551682
H	6.496604	0.145288	0.239959
C	5.703424	−1.62046	1.180593
H	6.674593	−2.06166	1.359433
C	4.545381	−2.29592	1.567577
H	4.613459	−3.26514	2.041983
C	3.291388	−1.73806	1.331313
H	2.399712	−2.28421	1.599765
C	1.86008	2.002525	−0.10936
C	2.006459	2.324372	−1.46821
H	1.918246	1.551481	−2.21787
C	2.279558	3.636448	−1.85331
H	2.391475	3.868486	−2.90348
C	2.402384	4.64164	−0.89508
H	2.61326	5.658392	−1.19765
C	2.249795	4.331235	0.456305
H	2.339836	5.106008	1.205698
C	1.977861	3.022032	0.849193
H	1.855642	2.801864	1.899239
C	0.704118	0.378849	2.038321
C	1.397637	0.460397	3.249068
H	2.477857	0.434287	3.256351
C	0.696573	0.539542	4.454078
H	1.239941	0.585849	5.387783
C	−3.18704	−0.48475	0.706047
C	−4.35386	0.187691	0.312454
H	−4.29308	1.143897	−0.18375

C	–5.6044	–0.38028	0.551652
H	–6.49659	0.145287	0.239899
C	–5.70343	–1.62043	1.180605
H	–6.67461	–2.06162	1.359449
C	–4.5454	–2.29588	1.567631
H	–4.61349	–3.26509	2.042074
C	–3.2914	–1.73804	1.331364
H	–2.39973	–2.28418	1.599853
C	–1.86008	2.002511	–0.10936
C	–2.00646	2.324358	–1.46821
H	–1.91824	1.551468	–2.21787
C	–2.27956	3.636433	–1.85331
H	–2.39148	3.86847	–2.90349
C	–2.4024	4.641624	–0.89508
H	–2.61328	5.658375	–1.19765
C	–2.24981	4.331218	0.456304
H	–2.33986	5.10599	1.205698
C	–1.97787	3.022016	0.849191
H	–1.85566	2.801849	1.899238
C	–0.70411	0.378844	2.038321
C	–1.39763	0.460386	3.249067
H	–2.47785	0.434266	3.256349
C	–0.69657	0.539537	4.454077
H	–1.23994	0.585838	5.387782

Table S17. Cartesian coordinates of the geometry-optimized $NiCl_3$(dppey) CT complex (**8a**).

Atom Type	x	y	z
Ni	–0.110938	0.533719	0.943799
Cl	1.439199	0.398839	2.537723
Cl	–1.84331	0.347985	2.314857
Cl	2.259021	–4.604297	–0.713854
P	–1.577865	0.819946	–0.678365
P	1.493666	0.606711	–0.580567
C	–2.394048	–0.736645	–1.222738
C	–3.222251	–0.759565	–2.358098
H	–3.437409	0.153969	–2.896786
C	–3.791419	–1.955323	–2.788912
H	–4.431125	–1.962491	–3.661081
C	–3.537945	–3.14104	–2.094783
H	–3.978563	–4.069358	–2.432066
C	–2.722088	–3.125272	–0.965334
H	–2.525	–4.038665	–0.422041
C	–2.153544	–1.928656	–0.525806
H	-1.541701	-1.916131	0.364116
C	-2.910525	2.068231	-0.482226
C	-4.184132	1.677882	-0.042594
H	-4.392052	0.636774	0.152175
C	-5.179463	2.630601	0.163518
H	-6.155769	2.316074	0.505648
C	-4.915515	3.982975	-0.053486
H	–5.688779	4.720528	0.112572
C	–3.647282	4.381826	–0.474404
H	–3.431287	5.42957	–0.633255
C	–2.648293	3.432324	–0.68332
H	–1.667564	3.768018	–0.990021
C	–0.623256	1.356351	–2.199293
H	–1.217933	1.228336	–3.104458
H	–0.385896	2.41711	–2.106249
C	0.670465	0.524259	–2.258736
H	1.333919	0.873501	–3.051013
H	0.417717	–0.517013	–2.46569
C	2.424233	2.198001	–0.624639
C	3.361228	2.457811	–1.638761

H	3.57914	1.707298	–2.387553
C	4.033645	3.676754	–1.680693
H	4.75573	3.865833	–2.463438
C	3.780424	4.649028	–0.710086
H	4.305809	5.593832	–0.741569
C	2.857872	4.395678	0.303352
H	2.667298	5.139672	1.064408
C	2.181191	3.175361	0.350206
H	1.49021	2.96916	1.154445
C	2.796718	–0.698887	–0.620276
C	3.773852	–0.71608	0.398665
H	3.742327	0.030426	1.176817
C	4.754957	–1.711188	0.433818
H	5.482674	–1.70847	1.232603
C	4.796172	–2.690806	–0.547069
H	5.551059	–3.46317	–0.5258
C	3.829723	–2.690997	–1.572087
H	3.923018	–3.371445	–2.404005
C	2.840052	–1.683797	–1.60551
H	2.114554	–1.717599	–2.402687

Table S18. Cartesian coordinates of the geometry-optimized $NiBr_3$(dppey) CT complex (**8e**).

Atom Type	x	y	z
Ni	–0.099998	0.514144	0.954595
Br	1.882248	–4.722217	0.172907
Br	–1.896107	0.363959	2.475348
Br	1.570795	0.242231	2.608871
P	–1.58001	0.823548	–0.660208
P	1.493009	0.612516	–0.58317
C	–2.361866	–0.740774	–1.235336
C	–3.166477	–0.769443	–2.387835
H	–3.389505	0.144344	–2.922571
C	–3.701683	–1.972193	–2.842333
H	–4.324048	–1.982895	–3.72692
C	–3.435451	–3.160375	–2.15722
H	–3.84882	–4.094061	–2.513614
C	–2.640735	–3.14025	–1.012924
H	–2.430089	–4.055168	–0.477517
C	–2.108417	–1.936321	–0.548714
H	–1.509949	–1.924493	0.350291
C	–2.924759	2.060844	–0.468387
C	–4.244605	1.665567	–0.210774
H	–4.492763	0.616947	–0.148352
C	–5.239826	2.621742	–0.01568
H	–6.253213	2.302975	0.185985
C	–4.929307	3.980215	–0.062897
H	–5.702406	4.719666	0.095051
C	–3.6151	4.382406	–0.302197
H	–3.364355	5.434113	–0.326885
C	–2.617146	3.430363	–0.4995
H	–1.60078	3.763973	–0.659525
C	–0.633315	1.39863	–2.173249
H	–1.234927	1.29022	–3.076437
H	–0.407539	2.459478	–2.053417
C	0.66536	0.580105	–2.26296
H	1.330412	0.965983	–3.036268
H	0.42792	–0.454114	–2.514347
C	2.424651	2.203824	–0.607459
C	3.350244	2.478464	–1.628628

H	3.562382	1.737411	–2.388163
C	4.019514	3.699432	–1.663415
H	4.73311	3.898676	–2.451362
C	3.77287	4.661084	–0.680757
H	4.294719	5.607959	–0.707761
C	2.860834	4.394292	0.33864
H	2.67468	5.129844	1.108933
C	2.189481	3.170888	0.379287
H	1.506259	2.956254	1.187822
C	2.77571	–0.705867	–0.648497
C	3.927819	–0.588305	0.151579
H	4.076573	0.294615	0.753275
C	4.879852	–1.610581	0.183381
H	5.752488	–1.503341	0.811956
C	4.705848	–2.756111	–0.583044
H	5.44062	–3.548039	–0.561233
C	3.562477	–2.888075	–1.384895
H	3.452782	–3.739366	–2.039511
C	2.599938	–1.863813	–1.410681
H	1.723261	–2.00518	–2.023892

H.2. TD-DFT

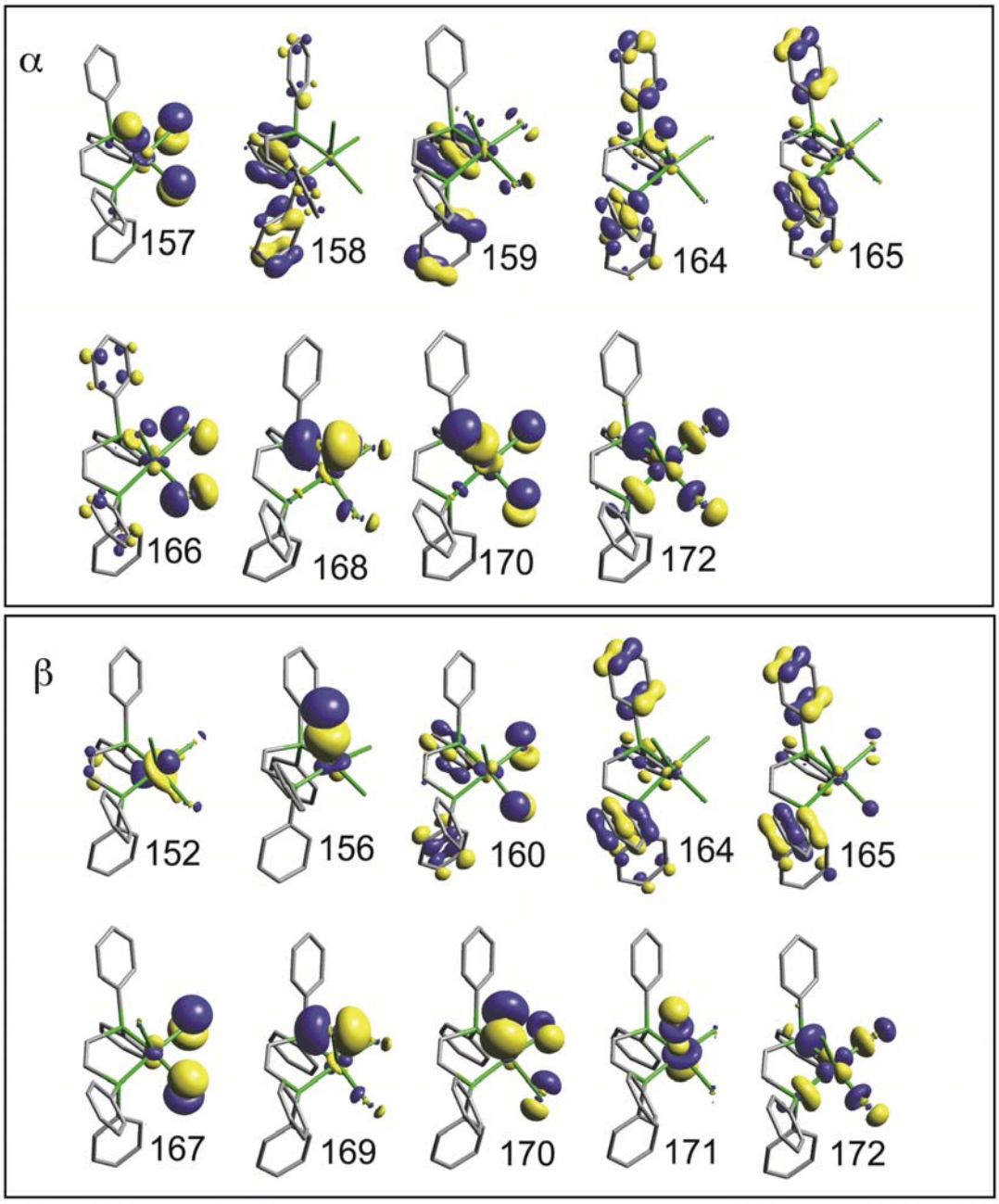

Figure S52. Representative molecular orbitals of $NiBr_3$(dppey) (**7f**). Note that state 7 above consists largely of β156 → β171.

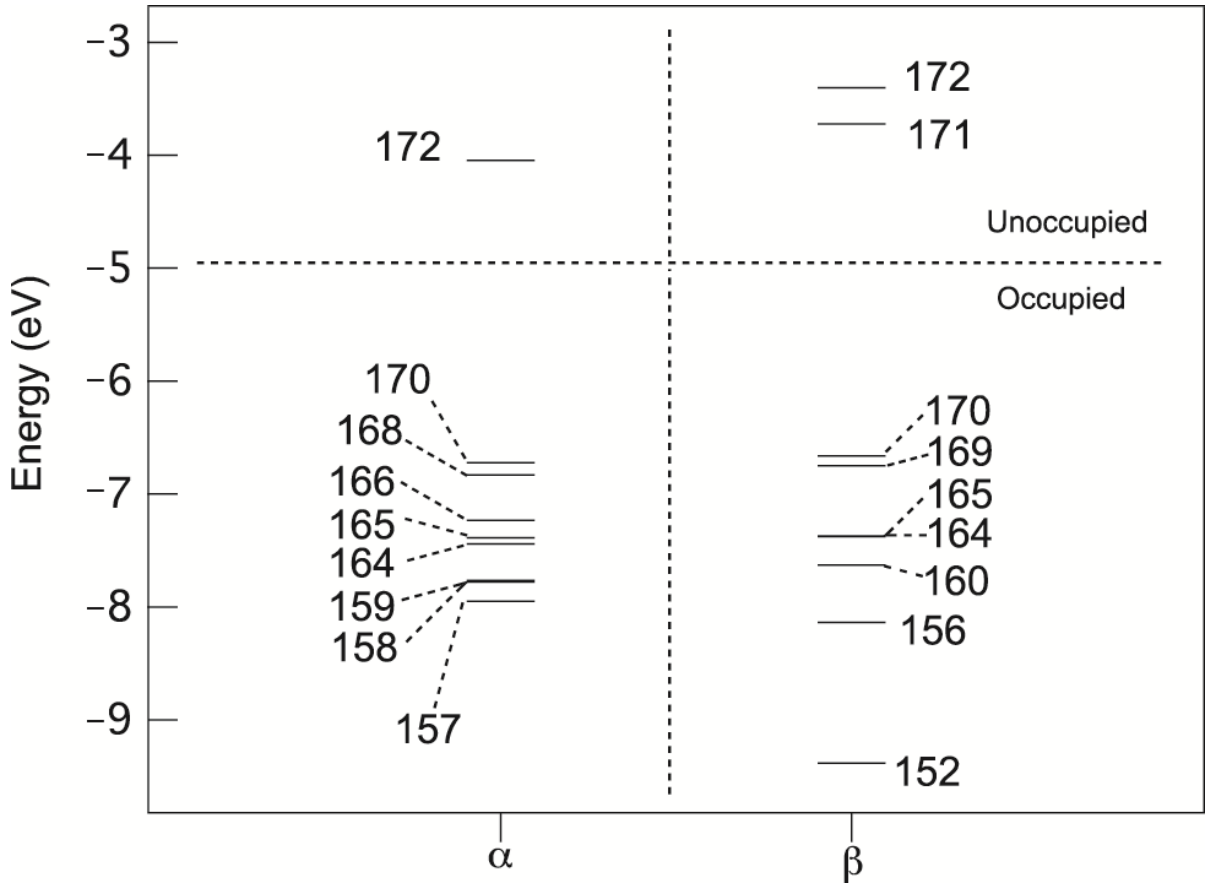

Figure S53. Energy levels of frontier molecular orbitals of $NiBr_3$(dppey) (**7f**).

Table S19. TD-DFT calculated transitions for $NiBr_3$(dppey) (**7f**), (DCM = CH_2Cl_2).

State	λ/nm	Energy/eV	*f*[a]	Contributions	Assignment
1	833	1.48	0.0099	170A → 172A (78%) 168A → 172A (10%)	α(pσ(ap)) → α(d_{x2-y2})
2	575	2.16	0.0246	169B → 172B (29%) 166A → 172A (17%) 168A → 172A (14%)	β(pπ(ap)) → β(d_{x2-y2})
3	493	2.51	0.0132	165A → 172A (48%) 170B → 172B (15%)	α(Phπ) → α((d_{x2-y2})
4	488	2.55	0.0064	157A → 172A (26%) 169B → 172B (21%)	α(pπ(dis)) → α(d_{x2-y2})
5	465	2.67	0.0138	164A → 172A (29%) 164B → 171B (19%) 157A → 172A (12%)	α(Phπ) → α(d_{x2-y2})
6	455	2.73	0.0738	164A → 172A (46%) 164B → 171B (23%)	α(Phπ) → α(d_{x2-y2})
7	440	2.82	0.0096	156B → 171B (30%) 152B → 171B (12%) 165B → 171B (12%)	β(pσ(ap)) → β(d_{z2})
8	435	2.85	0.0117	157A → 172A (18%) 159A → 172A (14%) 160A → 172B (13%) 165B → 172B (11%)	α(pπ (dis)) → α(d_{x2-y2}) + α(Phπ) → α(d_{x2-y2})
9	408	3.04	0.0055	158A → 172A (45%) 164B → 172B (12%)	α(Phπ) → α(d_{x2-y2})
10	398	3.11	0.0316	158A → 172A (16%) 164B → 172B (10%)	α(Phπ) → α(d_{x2-y2})

[a] Calculated transitions with oscillator strengths greater than 0.0050 are listed.

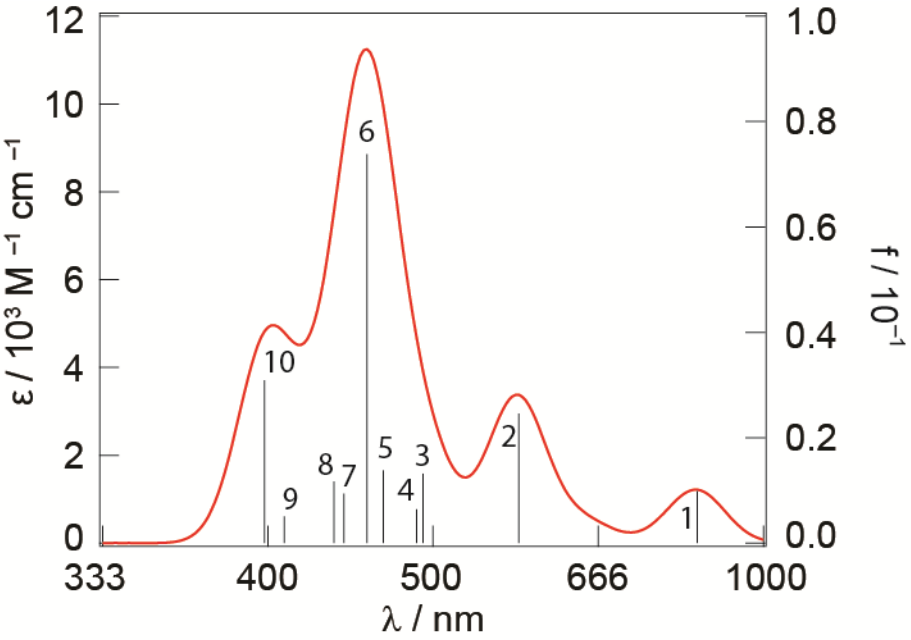

Figure S54. Relevant oscillators (oscillator strength > 0.02; solid black bars) from TD–DFT calculations for complex $NiBr_3$(dppey) (**7f**) with simulated absorption spectrum overlaid (solid red line).

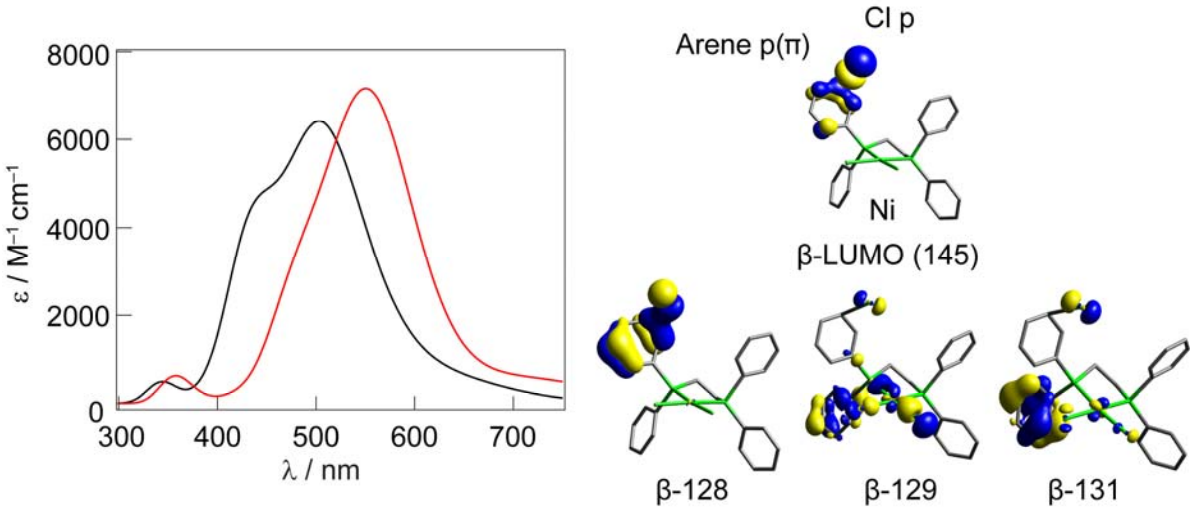

Figure S55. Computational results on the NiX_3(dppe) CT complexes. (Left) Gas phase TD-DFT calculated absorption spectra for $NiCl_3$(dppey) (**8a**), (black line) and $NiBr_3$(dppey) (**8e**), (red line). (Right) Major molecular orbitals involved in the formation of the absorption features observed around 500 nm for the Cl-based CT complexes. Donor orbitals are along the bottom right, and the acceptor β-LUMO is above right.

H.3. Correlation of Quantum Yield with Computed Ligand Donor Strength

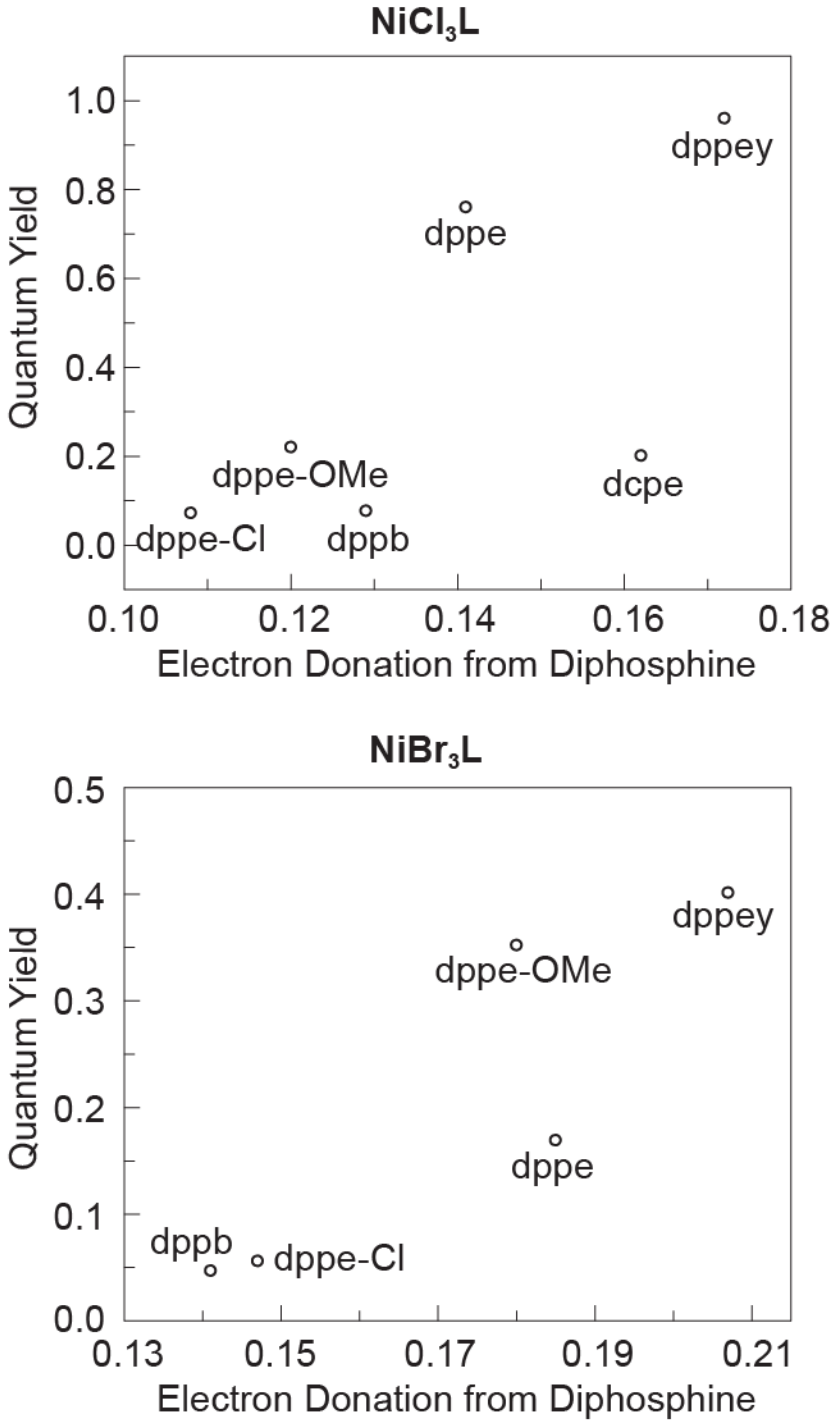

Figure S56. Plot of experimental quantum yield versus computed electron donation from the diphosphine backbone to the NiX_3 core.

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